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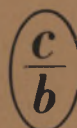
March, 1992

LITHOLOGY AND MINERAL RESOURCES

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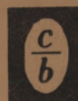
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CONNECTION OF HYDROTHERMAL ORE FORMATION WITH TECTONICS,
MAGMATISM, AND THE DEVELOPMENT HISTORY OF THE RED SEA RIFT
ZONE

G. Yu. Butuzova

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Analysis is carried out on the interrelations between the hydrothermal ore formation process, tectonics, magmatism, and stages in the development of the Red Sea rift. It is shown that maximum hydrothermal activity is coupled with the stage of transformation of continental crust to oceanic crust. A clearly expressed pulsational character is established for hydrothermal activity with extremely variable irregular periodicity at each discharge center. This is apparently caused by the functioning regime of small, separate, intermediate magmatic chambers.

It is known that deposits rich in iron, manganese, and polymetals are developed within the limits of the global system of rift zones of the world ocean, and that their formation is connected with active hydrothermal action.

The problem of hydrothermal-sedimentary ore genesis is extremely complex and diverse. Its solution requires consideration of a wide circle of questions such as: development of conditions for the origin and regularities in the localization of hydrothermal systems, the expansion of mechanisms for thermal solution formation, the formation of multicomponent mineral associations by their discharge, the establishment of natural environments most favorable to the concentration of ore material, and the estimation of the economic value of ore occurrences. One of the most important objects in this problem is also the establishment of space-time and cause-effect connections between hydrothermal activity and tectonics, magmatism, and the development of corresponding structures of the earth's crust.

In the most general view, analysis of this type of connection is generalized in the monograph of Rona [9]. This showed that hydrothermal mineralization may be formed in different tectonic environments, where favorable physical and chemical tectonic environments are created for hydrothermal convection. In recent years, detailed geologic-geophysical investigations have been conducted on individual segments of oceanic rifts with clearly expressed modern hydrothermal activity. These investigations made it possible to refine some features of the localization of discharge sources of underwater hydrotherms, their connection with tectonic structure, floor topography, stages of tectono-volcanic cycles, as well as with the type of underwater eruption and the petrochemistry of the bottom rocks.

Disregarding the significant progress in the development of the tectono-magmatic aspects of hydrothermal activity, many questions relating to the nature of actual interconnections between the ore forming process, tectonics, magmatism, and the evolution of corresponding structures are not completely clear, and they require supplemental data on the character of hydrothermal activity in oceanic spreading zones.

The Red Sea represents an extremely promising object for analysis of this type of interaction. Here, structural-tectonic and geomorphological inhomogeneity of the basement are combined, and they reflect different stages in the development of the rift system, the high intensity of the ore forming process, active magmatism, varied composition, degrees of ore content in the deposits, and the physical-chemical environments of ore material deposition. In addition, the Red Sea region is distinguished by good geophysical, lithologic-geochemical, and general geologic study. All of this makes it possible to consider the Red Sea as a reference polygon for the development of a model of hydrothermal-sedimentary ore genesis, of both its chemical-mineralogic, and its tectono-magmatic aspects.

STRUCTURE AND DEVELOPMENT HISTORY OF THE RED SEA RIFT

In agreement with modern ideas, the Red Sea is a typical example of an intercontinental rift zone, with oceanic crust forming in the axial parts and continental crust on the peri-

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phery; the continental crust thickness increases in the direction away from the rift axis. Morphologically, this is a narrow and deep "slot" 2000 km in extent, arising as a result of the movement of Arabian and African lithospheric plates, and representing a part of the earth's crust located in the early stages of oceanic basin opening.

The modern structure of the Red Sea does not agree with the structural plan of Precambrian and Paleozoic features, that is, it is not an inherited structure.

As a result of complex geologic-geophysical investigations, a clearly expressed inhomogeneity is established in the structure of the Red Sea rift zone. It appears in the morphologic, geophysical, and structural features of various parts of the sea floor, as well as in the character of magmatism and hydrothermal activity, which makes it possible to designate a completely defined zonality in the rift zone along its extent from southeast to northwest.

The southern part of the rift between 16 and $\sim 21^\circ$ N.lat. is characterized by development of a clearly expressed rift valley up to 60 km wide [31], which gradually tapers and transforms southwards into a chain of volcanic islands. The relief of this zone is strongly disjoint, with steep slopes and elevation differentials reaching 500 m. In the southern segment of the rift, oceanic crust is represented by a continuous band, and based on linear magnetic anomalies, its most ancient age is 5 million years [35], while to the north the crust is rejuvenated. In this part of the sea, 17 heat flow values were obtained within the limits of different geomorphological zones, including within the rift valley. Their average value is 134 mW/m^2 [20]. An axial zone (or inner rift) is distinguished in the limits of the rift valley. It is 4-5 km wide, with a central volcanic uplift (an extrusive zone 0.5-1.0 km wide) and framing basins. As a result of detailed investigations of the Red Sea rift at 18° N.lat., which were conducted in the course of the expedition of the Institute of Oceanology of the Academy of Sciences of the USSR, all details of its structure and geomorphology were ascertained, and its basic structural features were revealed [5, 8]. It is shown that the complex morphology of the axial zone is caused by numerous vertical fault-extensions, the maximum number of which is correlated to the margin of the axial zone. Transverse faults are developed in addition to the lengthwise faults. They divide the floor into numerous right angled blocks, and they represent incipient transform faults.

All of the structural elements and forms of relief in the axial zone have a clear linear orientation, parallel to the rift axis. In transverse section, the rift valley has a symmetric-stepwise structure. An upper tectonic step with a depth of 500-600 m is distinguished on its periphery. This step gradually transforms to a terrace, whose slope angle reaches $20-35^\circ$. Miocene evaporites are generally revealed in its walls. Lower tectonic terraces, divided by a system of high-angle faults (up to 60°) cross into the axial trough. The terrace surfaces are covered by sediments whose thickness decreases in the direction of the rift axis. In the most complexly disjoint axial zone, sediments are locally developed (principally in depressions), while on the elevated parts they are either very thin or completely absent.

In the northwest direction the rift valley becomes narrower, and the extrusive zone is discontinuous.

North of 21° N.lat. the oceanic crust is not developed in a single continuous band, but locally, discretely. Outcrops of oceanic basalts on the floor, whose age reaches <2 million years [12], are correlated to individual isolated basins, located amid more uplifted and generally more smoothed areas of Miocene evaporite development. It is proposed that places of basalt outcrop on the floor correspond to individual dispersed spreading centers.

Many investigators occupied with the tectonics of the Red Sea rift segment from ~ 21 to $\sim 23.5^\circ$ N.lat. consider it the region of oceanic crust formation, as a zone transitional from continental crust to oceanic crust. In only a few articles [22] the wide development in the rift valley of a transitional region of evaporite deposits and the absence of a continuous extrusive zone are connected not with presence there of continental crust there, but with the flow of plastic salts into the central part of the sea, the flow rate of which increases the spreading rate. Continuous development of oceanic type crust is thereby proposed in this segment.

Without going into similar analysis of geophysical material on the character of magnetic anomalies, in I. R. Cochran's opinion in agreement with rates of seismic wave propagation, and geothermal parameters, which as a result of detailed investigation of the Red Sea rift

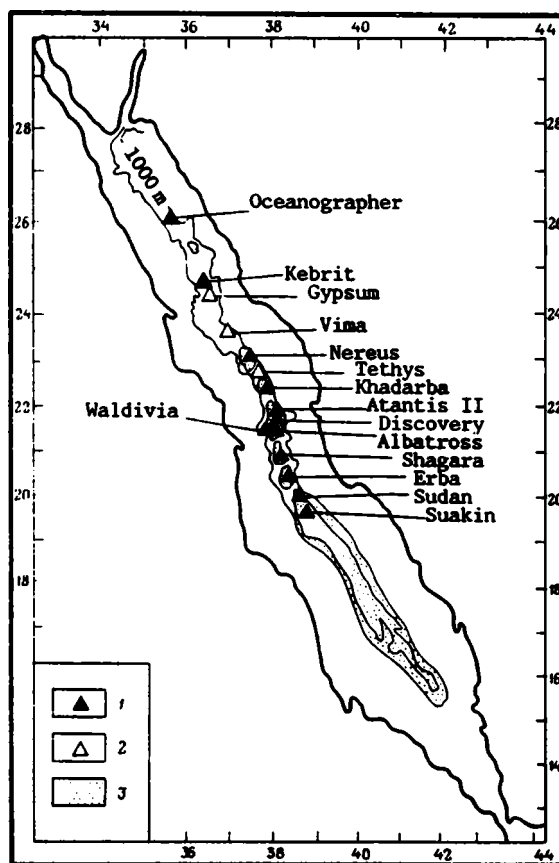


Fig. 1. Distribution in the axial part of the Red Sea rift of segments with oceanic crust (after [24]) and basins where hydrotherms generally discharge. 1) basins with brines; 2) basins without brines; 3) regions of oceanic crust development.

genesis led to the conclusion that the entire complex of geophysical data is in favor of the development of thinned, stretched continental crust with individual trough segments or windows of oceanic basalts in the transition zone [14, 15]. The distribution of basalt outcrops on the sea floor is shown in Fig. 1. If this is a continuous linearly elongated band in the southern segment, then to the north, the basalts form isolated segments whose number is notably reduced to the north. It is important to stress that in basins where basalts appear, thermal ore forming solutions are generally discharged, and sediments enriched by ore material are accumulated.

In transverse section the structure of the largest basins is similar to a typical profile across the axial zone of the southern part of the rift in general features. The Atlantis-II and Nereus basins may serve as examples of this structure type. Detailed geologic-geophysical investigations were conducted within their limits. Both basins have a clearly expressed rift valley, whose floor is made up of MORB-type tholeiite basalts. Based on magnetic anomalies, the age of the oceanic crust in the Nereus basin reaches <2 million years [12], while in the Atlantis-II basin (DSDP st. 227) it is 1.2 million years [21]. Extremely high values of conductive heat flow for the Red Sea are recorded in the deep water basins of the transition zone. Thus, in the Nereus basin (at a point with coordinates 23°07.75' N.lat., 27°18.5' E.long.) this value reaches 2233 mW/m² [12], while in the Atlantis-II basin (at a point with coordinates 21°37' N.lat., 38°08' E.long.) it reaches 3306 mW/m² [20]. In limits of deep water basins not only high heat flow is observed, but also wide dispersion of its values over small areas, which, as is known, assumes the presence of localized heat sources (magmatic chambers), and intensive heat output due to convective circulation of thermal solutions. In the Nereus basin heat flow varies from 2233 to 25 mW/m², in the Atlantis-II basin it varies from 3306 to ~100 mW/m². Beyond the limits of oceanic crust development, the heat flow is dispersed more evenly and comes to ~150 mW/m² [12]. The most active transform faults are concentrated and a large number of seismic activity epicenters

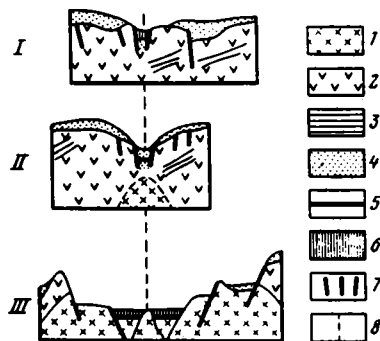


Fig. 2. A schematic image of seismic profiles illustrating development stages in the Red Sea rift (after [24]). I) Simple basin inside an evaporite sequence (Oceanographer, Kebrit); II) basin inside evaporites with near surface basaltic intrusions (Vima); III) basin with a central extrusive zone (Atlantis-II); 1) oceanic basalts; 2) evaporites; 3) sedimentary rocks inside evaporites; 4) Quaternary sediments; 5) ore muds; 6) brines; 7) faults; 8) spreading axis.

are recorded in the limits of the axial trough of the intermediate zone which partially encloses the northern termination of the southern segment (between 19 and 23° N.lat.), and here the maximum number of hydrothermal discharge sources is found.

In the opinion of most investigators, the northern segment of the Red Sea, from 23-24° N.lat. to the Suez canal, is a region with continental type crust which is significantly thinned but not faulted at the present time. Miocene evaporites form a practically continuous cover of the entire area of the floor here, including the central part. An axial depression 10-25 km wide, with an extent of ~500 km, and average depths of 1100-1200 m is developed on this segment. Here individual basins are localized inside the evaporite sequences.

The Vima basin is a typical example of this type of structure. Its axial valley is elongate along the extent of the rift. In this ~40 km long and 1611 m deep basin, an extrusive zone is absent, the floor is covered by evaporites, and the value of heat flow comes to ~200 mW/m² and is elevated relative to the background. In [31] it is shown that the average heat flow value in the northern segment of the rift regularly grows from 125 mW/m² at its margins to 250 mW/m² in the axial zone. No linear magnetic anomalies are formed here, and only single isolated isometric anomalies are recorded above places where oceanic basalts have intruded into the continental crust [22]. The northern part of the Red Sea rift is characterized by extremely weak seismic activity [18].

Spreading rates along the extent of the rift are also uneven. In the southern segment at 17° N.lat. they reach 1.49 cm/yr, in the Nereus basin region (~23° N.lat.) they reach 1.06, and at 25° N.lat. they reach 1 cm/yr [15].

Detailed magnetic investigations conducted by I. I. Belyaev and G. M. Valyashko in the southern segment (in the region of 18° N.lat.), made it possible to recognize significant changes in spreading rates over time, that is, the uneven, pulsational character of separation. It was shown that the maximum (up to 3 cm/yr) spreading rate on this segment corresponds to an age of 0.89-0.69 million years, while at the present time it has decreased to 1.04 cm/yr [5]. It is possible to propose that the value of 1.49 cm/yr cited by R. Girdler corresponds not to the modern stage, but is an average over a longer time period.

There are also successive variations in depth over the extent of the Red Sea rift. In the region of 15° N.lat. the average depth of the central extrusive zone reaches 1100 m, while at 18° N.lat. it is 1300 m, and at the boundary of the southern and central (transitional) segments, the extrusive zone is found at a depth of 2200-2300 m, and the maximum depth of the Red Sea (2850 m) is found here, in the region of the Suakin basin. More to the north, in the transitional zone, the central trough depths are reduced to a level of ~2000 m, while the depth of the individual basins reaches 2500 m. In the northern segment, where the extrusive zone is absent, sea depths average 1100-1200 m, and even in the axial basins they do not exceed 1600 m.

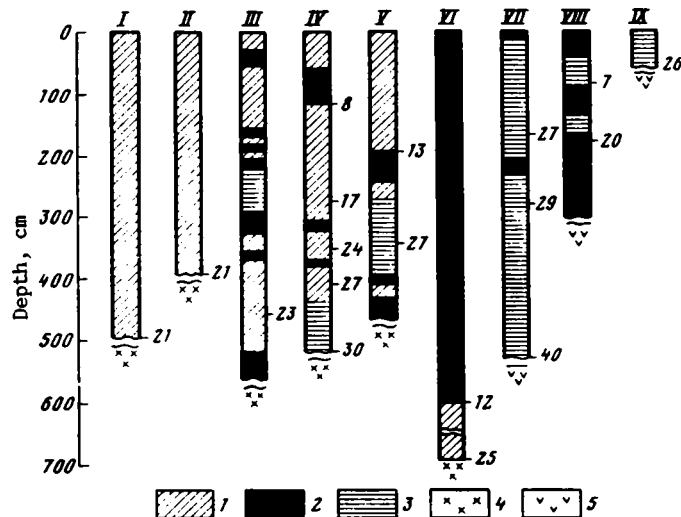


Fig. 3. Structure of sedimentary sections in deep water basins of the Red Sea rift zone. 1-3) sediment types: 1) metal-bearing; 2) ore-bearing; 3) biogenic-terrigenous, without hydrothermal material; 4) basalts; 5) evaporites; I-IX): basins: I) Suakin, II) Sudan; III) Erba; IV) Shagara; V) Albatross; VI) Atlantis-II; VII) Vima; VIII) Gypsum; IX) Kebrit. Numbers on columns are age in thousands of years.

The considered values of the Red Sea rift structure reflect the history of its development, the stages of rift genesis, and the evolution of spreading in its temporal succession. In agreement with abundant geological-geophysical data, the onset of rift genesis in the Red Sea region is dated at a time of 24-25 million years (Oligocene and Miocene boundary). As a result, a closed evaporite basin formed, where a thick (up to 7 km) sequence of salt-bearing deposits (Miocene evaporites) accumulated in the middle and late Miocene. Terraces formed at this time, which framed the contemporary axial trough. The early stage of rift genesis is not expressed in the magnetic field, and oceanic crust was not formed: only stretching and thinning of the continental crust occurred [22, 35, etc.]. Formation of the Miocene lead-zinc ore appearances which are developed on the western shore of the Red Sea are connected with this stage.

Splitting of the continental crust occurred in the Pliocene-Quaternary stage of spreading activation, whose development passed unevenly along the extent of the Red Sea rift. Spreading began in the southern part of the sea (to the north of the Bab-el-Mandeb strait) on the Miocene and Pliocene boundary nearly 5 million years ago, and gradually spread in a northwest direction. At this time oceanic water broke through across the Bab-el-Mandeb strait, and evaporitization ceased.

The subsequent development of rift genesis in Pliocene-Quaternary time is considered in [14, 15, 24]. In agreement with the proposed model, the initial stage is characterized by formation of an axial inner evaporite depression in the central part of the sea, which is accompanied by magmatism and the formation of individual basins, whose floors are as a rule made up of evaporites, that is, fracture of continental crust has still not occurred at this stage (Fig. 2I, II). Formation of the deepest and most complexly constructed basins with a central extrusive zone, active vulcanism, and hydrothermal activity occurs in the course of further development (see Fig. 2III). Evaporitic cover is absent from these segments (the continental crust is faulted), and oceanic basalts are developed on the floor. Localization of basins and the basaltic intrusions connected with them is controlled by the tectonic structure of the basement, most of all by the position of the transform faults. The basins and intrusive bodies connected with them are usually positioned within the limits of the axial depression in the middle part of the blocks between transformal fractures [15]. Rona also notes that deep water basins in the early stages of oceanic basin development generally lie not on the very same faults, but not far from them, along linear segments of the rift [9]. The similar character of basin localization is also stressed by their form: The basin's long axis is usually oriented along the spreading axis. It is proposed that variations in the morphometry and structures of tectonic depressions are controlled by the occurrence depth and by the volume of the magmatic chamber [15]. Deep water basins of the

axial zone are considered as discrete spreading segments, and single extended regions of normal oceanic crust are formed by their expansion and unification in the course of rift genesis [5, 15].

The separate stages of rift formation are clearly reflected in the modern structural plan of the Red Sea rift. Thus, its northern segment is found to be at the present moment in the latest stage of continental rift genesis, while young oceanic crust is forming in the transition zone, locally developing in the form of individual isolated segments, and the process of oceanic crust formation is already accomplished on the southern segment of the rift, with a most ancient age of ~5 million years.

HYDROTHERMAL ACTIVITY AND ITS CONNECTION WITH MAGMATISM

In the rift zone of the Red Sea, thermal solution discharge sources are as a rule localized within the limits of relatively deep water basins, which serve as traps for hydrothermal material entering the floor, and impede its dissemination over a wide area of the sea floor. The ore forming process is combined with simultaneous normal biogenic-terrigenous sedimentation processes. In similar conditions, the character of ore material distribution in sections of the sedimentary sequence rather completely reflects the regime of hydrothermal activity, its periodicity, and changes in time, permitting reliable reconstruction of the hydrothermal-sedimentary process and separation of the stages of hydrothermal activity into each actual discharge source, well as comparison between them.

As was already noted, the basic part of the basin with active manifestations of hydrothermal action is concentrated in the central (transitional) zone of the Red Sea rift. The southernmost depressions with metal-bearing deposits lie on a marginal part of the southern segment, in a region of closure of the oceanic crust development band, and in the northern part of the sea scarce ore manifestations are observed in basins where sediments lie immediately on evaporites (see Fig. 1).

For recognition of the specific course of the hydrothermal process in different parts of the Red Sea rift, it is appropriate to compare data on the structure of sections of hydrothermal-sedimentary deposits along the axial part of the rift in segments of varied structure. Sections of ten basins were taken for this type of comparison: Suakin, Sudan (southern segment of the rift), Atlantis-II, Erba, Albatross, Shagara (transitional zone), Vima, Gypsum, Kebrit (northern segment) (see Fig. 1). The similar lithologic-geochemical characteristics of deposits and features of ore genesis in Red Sea as a whole are considered in [1, 4, 7], the degree of ore content in the sediments was estimated with the aid of geochemical modules.

For our aims it is sufficient to consider the character of ore material distribution in sedimentary sections. They are schematically represented on Fig. 3, where three sediment varieties are distinguished: normal muds, which contain practically no hydrothermal components; metal-bearing deposits with an admixture mainly of the ore elements Fe and Mn no greater than 30%; and truly ore bearing accumulations, where hydrothermal material predominates [3].

It is understood that the first sediment variety is formed under conditions of the practical absence of hydrothermal discharge, the second forms under conditions of its low activity, and formation of ore horizons records a stage of significant hydrothermal activity.

From the presented data it follows that the deposits of southern basins (Suakin, Sudan) over their entire apparent thickness contain neither clearly expressed ore horizons nor normal sediments without an admixture of endogenic components, the number of which however significantly varies within the sedimentary section. This character of ore material distribution indicates the comparatively low intensity of hydrothermal activity, in the course of which sharp impulses of activity did not occur. At the same time, it is possible to consider the universal admixture of ore components as sign of continuous activity of a hydrothermal source over the course of a minimum of 20-30 thousand years (data from radiocarbon dating of sediments brought up in cores) [7]. Variations in the composition and quantity of ore components reflect some fluctuations in the intensity of the process.

Significantly different structures characterize the deposits of the transitional zone basin, where the maximum number of hydrotherm sources is concentrated. On the whole, they are more metal-bearing and are distinguished by an extremely uneven distribution of ore material, which is generally concentrated in individual packets, marking the stages of hydrothermal activity outbursts. The Atlantis-II basin lies in this zone, where the ore forming

process has a maximum intensity, and the deposits represent the single most economically valuable ore deposits or occurrences in the Red Sea. The great detail in the study of the sediments makes it possible to analyze the development of the hydrothermal process in the Atlantis-II basin from the moment of its initiation (20-25 thousand years ago) to the present time. In its early stages, the process moved rather sluggishly, and this was reflected in the accumulation of biogenic-terrigenous deposits with a significant admixture of ore components lying directly on the oceanic basalts; their upper age boundary is 12 thousand years (see Fig. 3). Beginning at this time, hydrothermal activity in basin was notably activated and muds with high ore material content have been accumulating up to the present. Judging by the complete series of lithologic-mineralogic, geochemical, and isotopic indicators, some decrease in activity is noted for the temporal interval from 8.5 to 6 thousand years. At the present moment this segment of the rift is found in a highly active stage of the hydrothermal process.

The Albatross, Shagara, and Erba basins lie not far from the Atlantis-II basin. They are characterized by a significantly different structure of their sedimentary sections (see Fig. 3). The presence of clearly expressed ore horizons of varied thickness, which are unevenly distributed in a mass of weakly metal-bearing or normal Red Sea muds is characteristic for them.

An important feature of the structure of the considered sections is the strict individuality in the character of ore material distribution even in closely adjacent basins: The nonagreement of ore horizon thicknesses, and the complete absence of their synchronicity are confirmed by both lithologic analysis and by radiometric dating.

Only one basin (Gypsum) where ore-bearing deposits predominate in the sedimentary section is found in the northern segment of the sea, since in the Vima basin the ore horizons are single and thin, and the sediments of the Kebrit and Oceanographer are filled by highly mineralized brines and contain practically no hydrothermal material. In this connection it is pertinent to note that the presence of brines in the basins is not a sign of deep hydrothermal discharge there, and the degree of mineralization of near bottom waters is determined to a significant extent by the dissolution of the evaporites comprising the sides of the depressions, their composition, thickness, area of exposed surfaces and the duration of contact with sea water, which in its turn depends on the basin morphology and the hydrodynamics of the near bottom waters. More detailed questions on the origin of the brines and their role in hydrothermal-sedimentary ore genesis are considered in [2, 10].

Thus, analysis of ore material distribution in the sedimentary sections of different parts of the sea floor makes it possible to assert that the episodicity of input and discharge of thermal solutions onto the floor and the pulsational character of the process are apparent over the entire expanse of the Red Sea rift. This feature is characteristic of all of the tectonically active zones of the global ocean, and comprises the fundamental law of hydrothermal activity in general. However the periodicity and duration of phases of hydrothermal activity at each actual discharge source (even if they lie close together) are incomparable among themselves, nonsynchronous, and varying in time, and this is clearly apparent in Red Sea ore genesis.

A similar regime of hydrothermal activity inevitably assumes the presence of individual isolated energy sources (intermediate magmatic chambers) under each of the segments of thermal solution discharge. Moreover, the very formation of basins, on the floor of which hydrotherms usually discharge, occurs as a result of the injection of basaltic intrusions [15, 24].

The direct connection of hydrothermal activity with the functioning of intermediate intracrustal magmatic chambers is not subject to doubt at the present time. Proof of this fact became possible thanks to wide utilization of the newest underwater technical means, of geophysical methods, and of petrochemical investigations in oceanographic research. Research of this type was conducted on individual segments of the rift zones of the global ocean, mainly in regions of contemporary intense hydrothermal activity, where "black smokers" exist and sulfide structures are formed (at 21° N.lat., 13° N.lat., and 20° S.lat. of the East Pacific rise, on active parts of the Mid-Atlantic ridge, and in the Galapagos regions [11, 17, 25-27, 37]. Mapping with the aid of underwater apparatus, geophysical investigations, and petrochemical testing showed that independent from spreading rates, the hydrothermal discharge sources are correlated to topographically complex depressions and on the whole elevated segments, lying between transformal faults. These segments are considered as in-

dividual segments of the spreading axis, under which intermediate magmatic chambers lie. It is established that active hydrothermal fields, are usually associated with regions of fluid lava development (sheet lavas). The predomination of fluid lavas over the more general pillow lavas is considered as an indicator of the presence of an intermediate magmatic chamber in its filling stage. This is confirmed by the emanation of a large quantity of thermal energy, and it accompanies the activation of hydrothermal convection [19, 29]. The opinion is also expressed that the presence of a magmatic chamber in the active stage of its life is also reflected in the petrochemical properties of the oceanic basalts [13]. In particular, segments coupled with chambers are usually comprised of the highest temperature (highly magnesian) basalts [27, 28], and sources of hydrothermal discharge are generally coupled to them.

Considering the undoubted connection of contemporary hydrothermal activity in the global ocean with magmatic processes, it is appropriate to consider briefly the existence of representation on sizes, form, and occurrence depths, as well as conditions of the localization and functioning of magmatic chambers which lie in the oceanic crust of rift systems. The opinion is expressed in [28] that the concept of sources existing in the oceanic crust where magma is accumulated until its extrusion onto the floor, is one of the central geologic ideas of this century. This idea is an important element of the generally accepted model oceanic crust formation. However, in spite of the evident importance of the problem of magmatism in the solution of many aspects of tectogenesis and hydrothermal ore formation, such questions as the functioning and development of magmatic sources, melt compositions, the real role and fraction of the fluid phase in hydrothermals, the cause of the episodicity of meltings and periodicity of volcano-magmatic events, and the determination of the geometric parameters of the chambers and their influence on hydrothermal activity are still extremely poorly studied and discussed, and still quite far from solution.

Considering a mechanism for the formation of individual spreading zones, some investigators have developed a model of a large (width to 30 km), stable magmatic chamber, while others have a preference for the existence of small reservoirs, localized discretely or contained in a "bunch" along the extent of the rift axis and acting asynchronously in time. The size (width) of this chamber type is estimated at values on the order of 1-2, maximum 5 km [17, 26, 37, etc.].

A later proposal on the character of intracrustal magmatic sources is confirmed by a combination of newest seismic data and thermal calculations, as well as the structure of ophiolite complexes. In our opinion, the above cited empirical data on the character of hydrothermal activity in the Red Sea, where the structure of the sedimentary sections clearly reflects the asynchronicity in the intensity and periodicity of the behavior of ore components in each individual source of hydrothermal discharge, also serves as a strong supplemental argument attesting to the independence of functioning in small, discontinuous, magmatic reservoirs.

Thus, the spatial and genetic connection of hydrothermal activity with small, isolated, intracrustal magmatic chambers may be considered as firmly established reality. The conditions controlling the regime of hydrothermal activity specifically are significantly less studied and understood, as was shown above for each actual discharge source. Apparently, the main cause of these types of small scale inhomogeneities is controlled by the character of the magmatic chambers (in their size, configuration, occurrence depth), and of course by the regime of their functioning (in the periodicity of new melt portion input, its crystallization, and the evolution of composition).

It is necessary to note that these questions are the least studied within the problems of magmatism and hydrothermal activity, mainly due to the absence of reliable methods and capacity for investigation. Nonetheless, general petrological and geochemical models of the development of near surface chambers exist, as well as some representations on the dependence of hydrothermal activity on the sizes of magmatic sources and their occurrence depths. As a rule, these representations and models bear a speculative character and in many cases they are based on theoretical calculations. Based on consideration of detailed petrologic investigations into the basalts of the Mid-Atlantic rift zone, [37] describes a scheme for the evolution of intracrustal magmatic chambers in which four stages of functioning are distinguished. In the first stage, the newly formed chamber is filled with nonfractionated primitive mantle melt; its filling occurs later, balanced by the processes of crystallization in an open system. The next stage is characterized by dominance of crystallization over filling,

and fractionation is developed towards the formation of Fe-Ti-bearing tholeiite basalts. Finally, in the last stage, input of new portions of melt ceases, the magma hardens, the source volume rapidly constricts, and the remaining melt becomes more acid.

Intensive extrusion of basaltic melt onto the floor occurs in a period of absence of a magmatic chamber under the rift valley. These periods are estimated at times on the order of 100-1000 years, while the periods of relative volcanic quiescence, corresponding to formation of intermediate chambers, are more prolonged (1-100 thousand years). In agreement with a model based on calculations of thermal diffusion, a magmatic chamber 1.6 km wide may exist for 30 thousand years, and then be completely crystallized in the following 100 thousand years [37].

In actuality, the regime of functioning of magmatic chambers is apparently considerably more complicated than this purely speculative and far from faultless scheme. As was already noted, it is possible to reconstruct this regime rather reliably through the hydrothermal activity, which in turn is clearly reflected in the structure of the sedimentary sections with absolute dating of the time of ore horizon formation. Analysis of actual sections uniquely demonstrates the extreme unevenness in the alternation of periods of sharp activity and relative quiescence for hydrothermal and corresponding magmatic activity.

Thus, in the Atlantis-II basin, the initial stage of the hydrothermal process was of low intensity and lasted 13 thousand years. In the course of the next 12 thousand years, activity increased sharply, while a period (2-2.5 thousand years) of notably decreased activity is noted on its background. In other basins (Tethys, Shagara, Albatross), stages of high intensity hydrothermal discharge is measured by times on the order of 1 thousand years, with a maximum of 4 thousand years. The periods of relative quiescence dividing them are somewhat more prolonged (tentatively to 10 thousand years), and while in the course of these periods hydrothermal activity may at some time completely cease, its intensity also varies widely.

Thus, analysis of actual material indicates that the relations of the duration of varying degrees of activity in the ore process, and the recurrence intervals of these events, are extremely varied, uneven, and specific for each actual discharge source.

The complex character of the variability in hydrothermal activity and the wide variation in its periodicity over the course of short intervals hinder the analysis of connections between hydrothermal-sedimentary ore genesis and the evolution of magmatic sources, for definite stages of their development.

Moreover, the empirically recognized coupling of contemporary hydrothermal activity with the development of high temperature (high magnesian) fluid lavas on the floor makes it possible to propose that hydrothermal activity accompanies the early stages of magmatic chamber evolution, or stages of its additional feeding by new portions of melt.

Investigation into the Skaergaard intrusive massif (eastern Greenland), which is considered the reference ancient magmatic chamber, is extremely interesting for the understanding of many important details of the hydrothermal processes connected with magmatic reservoirs. The results of these investigations are published in [33, 38]. The excellent exposure, complete section, and good preservation permit the detailed study of the form, size, and occurrence depth, as well as the relations of mineral, chemical, and isotopic composition of material in the intrusion's section. This served as a base for the reconstruction of the pluton's evolution, and for recognition of actual relations between magmatic and hydrothermal phenomena with consideration of the temperature, pressure, fluid flow, and permeability of surrounding rock.

The proposed model conjectures that a large quantity of a fluid phase is released from the pluton into the surrounding rock, whose permeability reaches 10^{-3} mD [33]. Corresponding calculations showed that in the early stages in the life of the magmatic source (~50 thousand years), hydrothermal circulation was limited by the surrounding rocks from their contact with the melt, while an average magnitude of fluid flow directed from the pluton reaches $5 \cdot 10^{-6}$ g·cm⁻²/sec, and the overall fluid flow over 50 thousand years is estimated at 500 kg·cm⁻².

The maximum thermal anomalies arising as a result of heat and mass transport from the source appear in the high heat flow values (~2000 mW/m²) and are observed at the 20-30 thousand year interval. Ionic diffusion of water into the pluton occurs with further cooling and recrystallization of the melt, and this is reflected in alteration of the isotopic

composition of oxygen in different silicate phases. The time for complete crystallization of the magmatic chamber is estimated at ~200 thousand years.

The above noted local differences in the level and periodicity of hydrothermal activity are probably controlled not only by the functioning regime of the intermediate chambers, but also to a significant degree by their sizes, configurations, and occurrence depths.

It is difficult to determine the geometry of magmatic sources in contemporary rift zones due to the absence of reliable geophysical methods. An opinion is expressed in [23] on the connection of volcanic periodicity and intrusion implantation with the form of the magmatic chamber; it is proposed that the narrower the source, the more there will be volcanic extrusion and filling of the chamber by new portions of melt, which correspondingly influences the periodicity of hydrothermal discharge activity.

The occurrence depth of magmatic chambers is rather reliably recorded with the aid of the newest seismic methods. By these data, the chamber roofs in the oceanic crust of modern rift zones usually lie at a depth on the order of 1-5 km [17 etc.]. The differing depths of the reservoirs create differing conditions of heat supply to the underground fluids, and this is accompanied by variations in the effects of their discharge. Hydrothermal circulation connected with deeply occurring chambers is characterized by relatively low temperature gradients, comparatively weak intensity, and great durations (on the order of 10-100 thousand years). High intensity systems arise for shallow source occurrences and high temperature gradients. Their periods of active life are shorter term (1-100 years) [9]. This character of hydrothermal activity is connected with a high rate of heat output which exceeds the rate of input into reservoir of new portions of magmatic melt, in other words, the higher the temperature and output of the source, the more rapidly the source's heat is dispersed and the shorter the period of extrusion of ore-bearing solutions. In its turn, hydrothermal circulation significantly hastens magma crystallization, thereby shortening the life of the magmatic chamber. Scales of heat output are recorded in values of convective heat flow and its dispersion.

The above considered features of the hydrothermal process over the extent of the Red Sea rift make it possible to propose that in the transition zone, where the basin deposits are on the whole characterized by high metal content and the presence of numerous individual ore horizons, the modern sources of hydrothermal discharge are coupled with shallow magmatic sources.

In the southern segment of the rift, where ore appearances are detected only in the closure region of the zone of continuous oceanic crust development, and where the deposits are characterized by comparatively low metal content and continuous prolonged source activity, the hydrothermal circulation is apparently connected with more deeply occurring single chambers.

Reliable signs of modern active hydrothermal activity are not detected to the south of the Suakin basin.* Extremely weakly expressed geochemical anomalies were noted by detailed chemical testing of sediments at 18° N.lat., close to the rift axis. Their recognition appeared possible only with the help of several not completely reliable geochemical modules [7]. The comparatively even and on the whole low heat flow values attest in favor of the absence of modern active hydrothermal discharge from the southern segment. Moreover, this part of the rift is characterized by high intensity of magma development [6], and in agreement with the general model of magmatic development, this indicates the absence of intermediate magmatic chambers under the rift valley.

If the noted correlation between maximum hydrothermal activity and a definite stage of rift formation in the Red Sea is genetically valid and not by chance, then it is logical to anticipate ore manifestations close to the modern zone in the mineral deposits of the southern segment. Analysis of deep water drilling data showed that in well 328 which lies 40-50 km west of the modern axial trough (coordinates 19°05.16' N.lat., 39°00.2' E.long.), at the

*An ore structure 20-25 cm high, formed at 18° N.lat. is described in [7, 8]. It is considered a hydrothermal formation. However, both the paragenesis of the minerals comprising it and features of its geochemistry are not inherent to hydrothermal manifestations at rift zones that are widely known at present time. From the point of view of the hydrothermal process, the presence inside the ore structure of geometrically parallel body (a parallelepiped 12 × 6 × 1.5 cm in size) does not yield to interpretation. It is composed of Fe phosphide, Mn sulfide, and anthracolite, as well as significantly enriched in such elements not characteristic of hydrothermal formations as Ni and Cr.

very top of the Miocene deposits, on its boundary with the Pliocene, a shale-anhydrite breccia occurs which is sharply enriched in sulfides of zinc (sphalerite) and iron (pyrite), as well as in manganese (to 1%). The zinc content in the rocks reaches 5%, and apart from Zn, Fe, and Mn, concentrations of Cu, Pb, and Cd are significantly increased. The value of $\delta^{34}\text{S}$ of the sulfides reaches +2.4% [30]. In other words, the complex of mineralogic-geochemical and isotopic features of ore mineralization whose age is equal to 5 million years completely corresponds to the young ore accumulations of the modern transitional zone and it is particularly close to the deposits of the Atlantis-II basin. It is possible to propose that hydrothermal mineralization in the mineral sediments of the southern part of the sea is distributed more widely, however limitations in the deep water drilling points do not make it possible to judge more definitely on the localization and scales of ore appearances in the past. Nonetheless, existing indicators of high temperature hydrotherms do not contradict the proposed connection of active hydrothermal activity in earlier stages of Red Sea ore genesis with stages of continental crust destruction and its transformation into oceanic crust, which corresponds to the modern transition zone.

In what genetic sense is a space-time connection empirically established between the defined stages of rift genesis and hydrothermal activity in the Red Sea?

It is widely known that modern hydrothermal systems are correlated to the global system of rift zones, which are found in various stages of development. The general regularity in the spatial distribution of hydrothermal discharge sources involves their sporadic nature and the unevenness of their localization along the axial part of the rifts. In recent years, with the aid of detailed geologic-geophysical investigations, establishment of clearly expressed inhomogeneities in the axial zone structures along the extent of rift systems was successful. Individual spreading segments are distinguished. They are as a rule divided by transform faults [19, 27, 29, 37, etc]. It is important to note that sources of hydrothermal discharge are correlated not to the faults, as was earlier thought, but to the segments between them, and not to each segment of spreading, but only to the magmatically active segments, under which lie intermediate chambers in active stages of development - to the so called neovolcanic zones. As geologic-geophysical investigations have shown, all segments of modern high temperature hydrothermal activity in developed oceanic rifts are coupled with the neovolcanic zones [26, 34, etc.].

Thus, tectonic position not in and of itself controls the localization of hydrothermal systems and the magmatic processes connected with them: penetration of magmatic melts into the crust, which serves as the energetic and material basis for heat and mass transfer, as well as for hydrothermal convection.

The above cited data on the Red Sea shows that in the course of oceanic rift genesis (in its early stages), the processes of transformation of continental crust into oceanic type crust are accompanied by high seismic tension, intense magmatism, and high temperature thermal activity.

In conditions of developing rifts, hydrothermal activity recommences with activation of magmatic processes in the neovolcanic zones. This is caused by the general periodicity of volcano-magmatic cycles, the causes of which are still insufficiently clear. In the opinions of some authors [6], one of the causes of the episodicity of mantle meltings is connected with a periodic lowering of pressure occurring as a result of tectonic causes, in particular the uneven separation of lithospheric plates.

Considering the tectono-magmatic aspects of hydrothermal system localizations, we will dwell briefly on the question of connection of hydrothermal ore genesis with spreading rates.

It is traditionally understood that the scales and intensities of hydrothermal activity depend directly on the spreading rate. However, such a dependence does not appear in analysis of the distribution of hydrothermal discharge sources and its scales and intensity in the rift zones of the world ocean. We will cite a few examples. Thus, the spreading rate varies from 5 (at 21° N.lat.) to 16 cm/yr (at 20° N.lat.) in the limits of the EPR on segments of high temperature hydrothermal discharge with "black smokers" and polymetallic sulfides [19]. Sulfide hydrothermal structures and "black smokers" were discovered not long ago in a slow spreading region of the Mid-Atlantic ridge within the limits of the TAG geothermal field at 26° N.lat. [36] and at 23°22' N.lat., 25 km south of the Kein fracture [16]. The forms and scales of hydrothermal activity on these segments are completely comparable, and sometimes exceed the corresponding processes in high spreading regions of the EPR.

As a result of detailed analysis of hydrothermal deposits from a core drilled on the western slope of the EPR with accurate age indicators, it was concluded that there is a complete absence of correlation between the stages of activization of hydrothermal action and changes in spreading rates [32].

Finally, as was shown above, within the limits of the Red Sea rift, localization of the most active sources of hydrothermal discharge is not connected with the segments with maximum spreading rates.

Other evidence for the absence of a direct dependence of hydrothermal activity on spreading rate is given by calculation of convective heat output, and in agreement with this the total value of convective heat flow in rift zones with low spreading rates is higher than in ridges with high spreading rates, and accordingly comes $15.1 \cdot 10^8$ cal/cm² [39].

At first view, the cited facts contradict the widely held hypothesis on the direct dependence of the hydrothermal ore-forming process on spreading rates.

However it is evident that data existing at this time are clearly insufficient for objective proof or disproof of this principal position. The matter includes not only the prospective discovery of new ore manifestations and a possible correction of the observed of new ore manifestations and a possible correction of the observed picture of their distribution on the ocean floor. The most vulnerable concept is found in the circumstance that estimation of spreading rates in the oceanic rifts determined by magnetic anomalies is given for large intervals of geologic time, and it represents an integrated value, where possible existing variations and jumps in separation are leveled and averaged. A combined study of these phenomena at a single time scale is necessary for a sure solution of the question on the connection of underwater hydrothermal ore genesis with spreading rates.

It is possible to state the following general positions based on a summing up of the considered data on the localization of hydrothermal systems, their functioning regime, and connection with tectonics and magmatism in the Red Sea rift zone, as well as by analysis of literature materials on other oceanic rifts.

1. Tectonic control of hydrothermal-sedimentary ore genesis takes place in a general form through magmatic processes connected with tectonics.

2. The presence of magmatogenic heat and mass carriers, that is, intermediate intracrustal magmatic chambers, is the determining factor for circulation of thermal ore-forming solutions.

3. Hydrothermal activity in the rift zones has a clearly expressed pulsational character with extremely variable and irregular periodicity at each source of discharge. This is apparently caused mainly by the functioning regime of shallow, discrete, intermediate chambers, as well as by their form, sizes and occurrence depths.

4. In the Red Sea rift zone, maximum hydrothermal activity is coupled with the early stages of oceanic rift genesis, with the stage of transformation of continental crust into oceanic crust, and with the tectonics of the destruction and formation of individual spreading zones. This is combined with high seismic activity, abundant intermediate magmatic chambers, highest values of heat flow, and its highest dispersion. Within the limits of developed rifts in midocean ridges, the sources of hydrothermal discharge are correlated to the magmatic activity of the segments, to the so called neovolcanic zones.

In conclusion we note that the combination of geologic, geophysical, petrochemical, and lithologic-geochemical data uniquely attests to the existence of space-time and cause-effect relationships between tectonics, magmatism, hydrothermal activity, and ore formation in the rift zones of the global ocean. This indicates the advisability of joint analysis of these phenomena within the limits of the overall conception of oceanic tectogenesis.

Prospective paths for our further investigation are also represented by detailed comparison of the fine geochemical and crystallochemical features of the ocean floor basalts with the specifics of hydrothermal activity, its intensity, periodicity, temperature regime, and establishment of the nature of petrochemical variations in the basalts in dependence on the regime of hydrothermal discharge and functioning of the magmatic source. Similar investigations will promote understanding of the very mechanism of hydrotherm formation and can lead to solution of one of the cardinal problems of hydrothermal-sedimentary ore genesis: the problem of ore material sources.

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SEVERAL FEATURES OF LATE QUATERNARY SEDIMENT ACCUMULATION
IN THE BLACK SEA. REPORT 1: BOTTOM DEPOSITS AND DISTRIBUTION
FEATURES OF THE DIAGENETICS OF THE ACTIVE COMPONENTS

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New factual material is presented on the distribution of reactive forms of iron [pyrite, hydrotroilite, and nonsulfide forms of Fe(II) and Fe(III)], as well as C_{org} and $CaCO_3$, in the section of late Quaternary deposits of various zones of the sea.

Modern representations on the geochemical evolution of the Black Sea in late Quaternary time, which are due to the efforts of Strakhov, are based to a significant degree on analysis of the distribution in sediments of basic diagenetics of the active components: iron and sulfur compounds. These elements, by virtue of their clearly expressed oxidation-reduction properties, form a series of chemical and mineral forms, the degree of development and the mutual relations of which largely reflect the conditions of sediment formation. A necessary direction for the geochemical investigation of the Black Sea at the present time is the refinement, close examination, and correction of the qualitative model worked out by Strakhov for basin development [5, 6]. This may be assured, in particular, by further, more detailed study of the distribution of these forms in late Quaternary deposits, and expansion of information included in them.

This article describes the representation and analysis of new factual material, including nine vertical sections of sedimentary sequence taken in different regions and morphometric zones of the sea with the help of a geologic core (TBD) during the eighth voyage of the NIS "Vityaz" (1984).

The obtained data characterize the deposits of the central part of the western and eastern chalistase, the slope-foot of the northwest continental slope, various depths of the eastern, southern, and northern slopes, as well as sediments of the lower part of the Kalamitic shelf of the Crimea. The station distribution is shown in Fig. 1.

Figures 2-5 show profiles of the distribution of C_{org} and $CaCO_3$ (% of dry sediment weight), total and reactive forms of iron in computation to noncarbonate material; pyrite, sulfide (Fe hydrotroilite), and nonsulfide Fe(II) and Fe(III) forms, as well as the distribution of these forms in the composition of their sum (ΣFe_{reac}). The methodological part, the data of the chemical-analytical determination and their detailed comparative descriptions are found in [3].

The completed sections are examined within the framework of a traditional general scheme of stratigraphic divisions in the investigated sedimentary sequence into the Novoevksinsk, Ancient Black Sea, and Recent deposits [4, 5]. In addition, it is appropriate to use the trial lithologic division to divide the Novoevksinsk sediments into three subhorizons (see Figs. 2-5): early (W^1_{II}), middle (hydrotroilitic, (W^2_{II})), and late Novoevksinsk (lower Holocene, (Hl_I)) [7]. It is necessary to note, however, that this division, which is based mainly on spore-pollen analysis data, is not indisputable at the present time, bears a largely preliminary character, and requires further refinement. Nonetheless, it is rather promising, particularly for the plan of reconstructing the formation conditions for the complex polycomponent sulfide mineralization in the Novoevksinsk deposits, since the lithologic-mineralogic aspect of these sediments are connected with event of the end of the glacial period, which must have influenced the composition of the complex of reactive iron forms in the Novoevksinsk basin. The lithologic features and utilization of this stratigraphic scheme for the description of sediments from several regions of the sea, also including a series of the considered sections, are contained in [7, 8].

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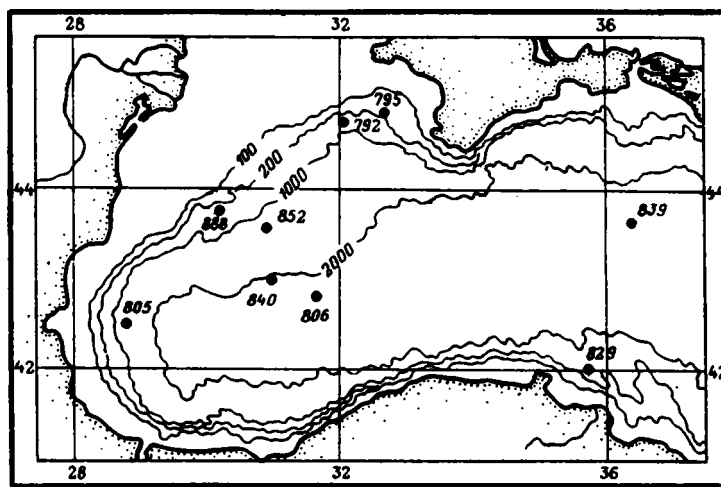


Fig. 1. Scheme of distribution of test sample stations.

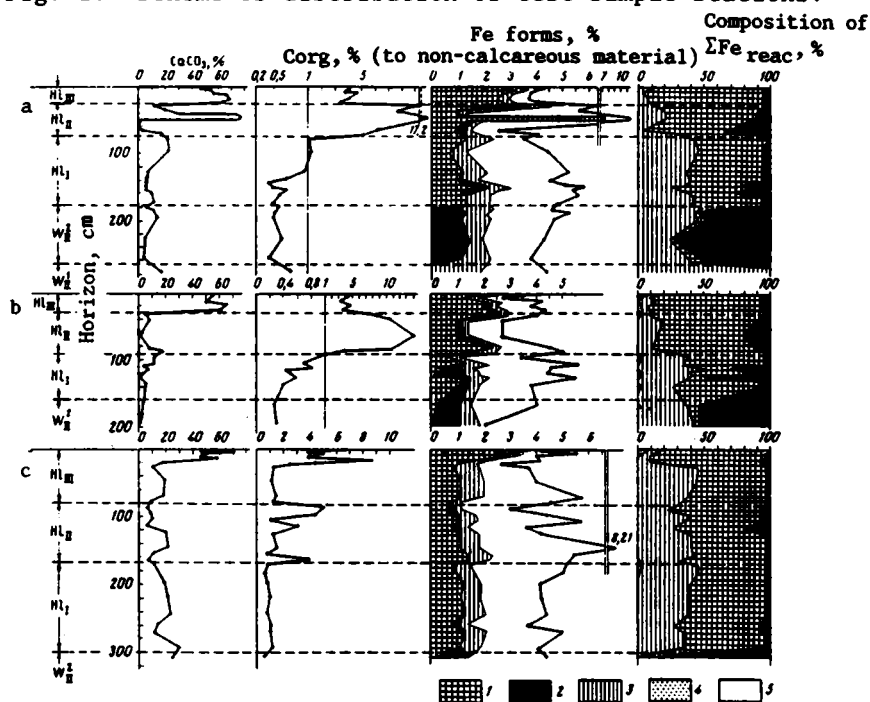


Fig. 2. Distribution of C_{org} , $CaCO_3$, and forms of iron in pelagic deposits: a) st. 840, depth 2125 m ($42^{\circ}55.6'$ N.lat., $30^{\circ}58.4'$ E.long.); b) st. 806, depth 2100 m ($42^{\circ}46.2'$ N.lat., $31^{\circ}39.0'$ E.long.); c) st. 839, depth 2160 m ($43^{\circ}33.0'$ N.lat., $36^{\circ}25.5'$ E.long.). Stratigraphic horizons: W_1^{II} early Novoevksinsk (middle Wurmian); W_2^{II} middle Novoevksinsk (late Wurmian); $H1_I$ late Novoevksinsk (lower Holocene); $H1_{II}$ Ancient Black Sea (middle Holocene); $H1_{III}$ Recent (upper Holocene). Iron forms: 1) Fe pyrite; 2) Fe hydrotroilite; 3) nonsulfide Fe(II); 4) reactive Fe(III); 5) detrital forms.

It is not appropriate to relate the proposed results of geochemical investigations to the bathymetric position of sediments, describing the columns in the direction from the bottom upwards. This reflects the sequential succession in the sediment formation conditions. The overall lithologic characteristics of the deposits are based on data from the report of the lithologic order of the expedition (A. V. Komarov, Southern Department of the Institute of Oceanology of the Academy of Sciences of the USSR).

NOVOEVKSINSK DEPOSITS

We investigated the Novoevksinsk sediments from different regions of the sea. They are generally represented by light grey carbonate-clay muds of blueish and greenish tints, homo-

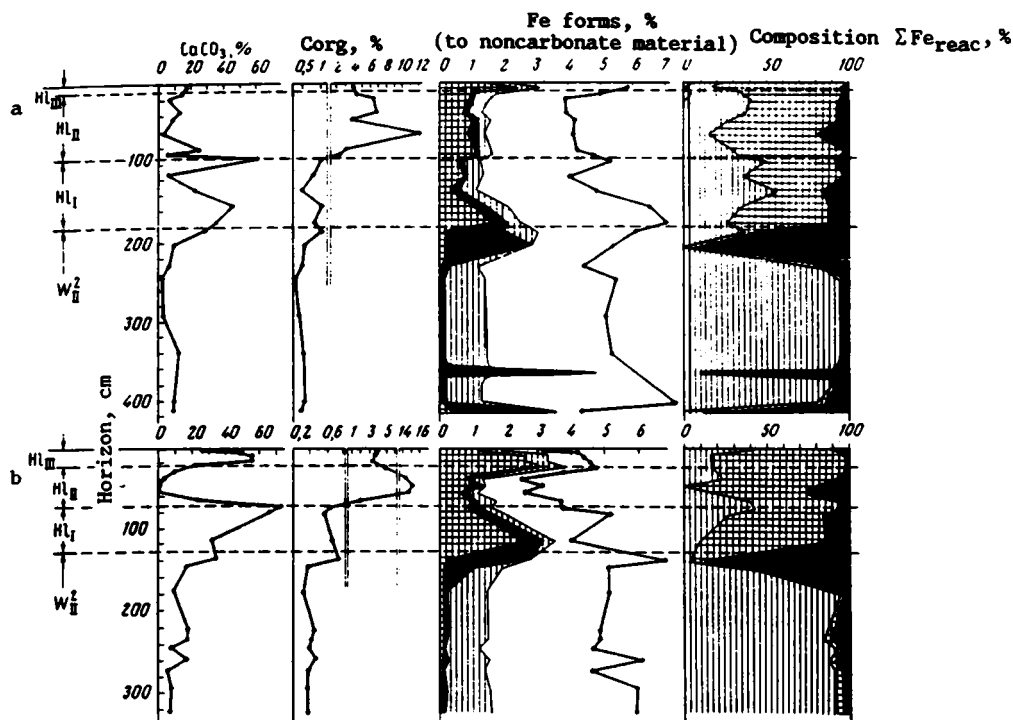


Fig. 3. Distribution of C_{org} , $CaCO_3$, and iron forms in deposits of the lower part of the western slope: a) st. 805, depth 1585 m ($42^{\circ}28.1'$ N.lat., $28^{\circ}51.4'$ E.long.); b) st. 852, depth 1333 m ($43^{\circ}32.5'$ N.lat., $30^{\circ}53.6'$ E.long.). Legend as in Fig. 2.

geneous or unclearly expressed bedding, and black particles of hydrotroilite mineralization unevenly distributed through the section.

Early Novoevksinsk Glacial Deposits (W^1_{II}), which underlie the hydrotroilite horizon, are characterized by only one sample of blue-grey homogeneous weakly carbonate-clay mud, taken in sediments at the slope-foot of the northwest slope (see Fig. 1, 2a, st. 840, horizon 270-280 m). The sediment is distinguished by an extremely low reduced sulfur content, in spite of the significant C_{org} content (0.72%). Sulfur pyrite (0.020%) is the basic form added to the derived reduced sulfur (ΣS_{H_2S}) which comprises 0.023%, although all remnant forms (S_{org} 0.008%, S^0 0.001%, S^{2-} 0.001%) are also present in negligible quantities. The total iron content comes to 3.6-4% and the sum of Fe_{reac} (1.4-1.8%) in practice completely represents nonsulfide Fe(II). The concentration of sulfate sulfur in the muddy water is equal to 0.106 mg/ml.

Middle Novoevksinsk Deposits (W^2_{II}) may be quite completely characterized by the entire available sections, with the exclusion of st. 839 (see Fig. 2c) of the eastern chalistase, where they are represented only by the top of a 10 centimeter layer of black, highly dispersed, clay-carbonate mud. The character of the distribution of hydrotroilite mineralization corresponds in its basic features to observations discussed in the literature [4, 7]. A single horizon, completely stained by sulfides, is detected in the pelagic zone of the western part of the sea (st. 806, 840), however, it is also detected in the upper part of the southern slope (st. 829). Another variation of stratification, which consists of several interbeds clearly enriched by sulfides on a background of overall insignificant hydrotroilite content, occurs on the lower parts of the slope (see Fig. 3a, st. 805), as well as the shelf (see Fig. 5b), st. 795). The overall thickness of the middle Novoevksinsk horizon on the shelf and slope is significantly greater than in the pelagic zone.

The transition from the early to middle Novoevksinsk horizon is expressed quite clearly. From the results of sediment analysis for st. 840 (see Fig. 2a), along with the appearance of significant quantities of sulfide sulfur (S^{2-} up to 1%), it is accompanied by a noted decrease in C_{org} content (from 0.72 to 0.4%), a fall in carbonate (from 18 to 5-9.3%), a decrease of total iron, and an increase of ΣFe_{reac} in its composition. It is also necessary to note some decrease in the concentration of sulfate in mud waters (from 0.106 to 0.82 and even to 0.088 mg/ml SSO_4^{2-}).

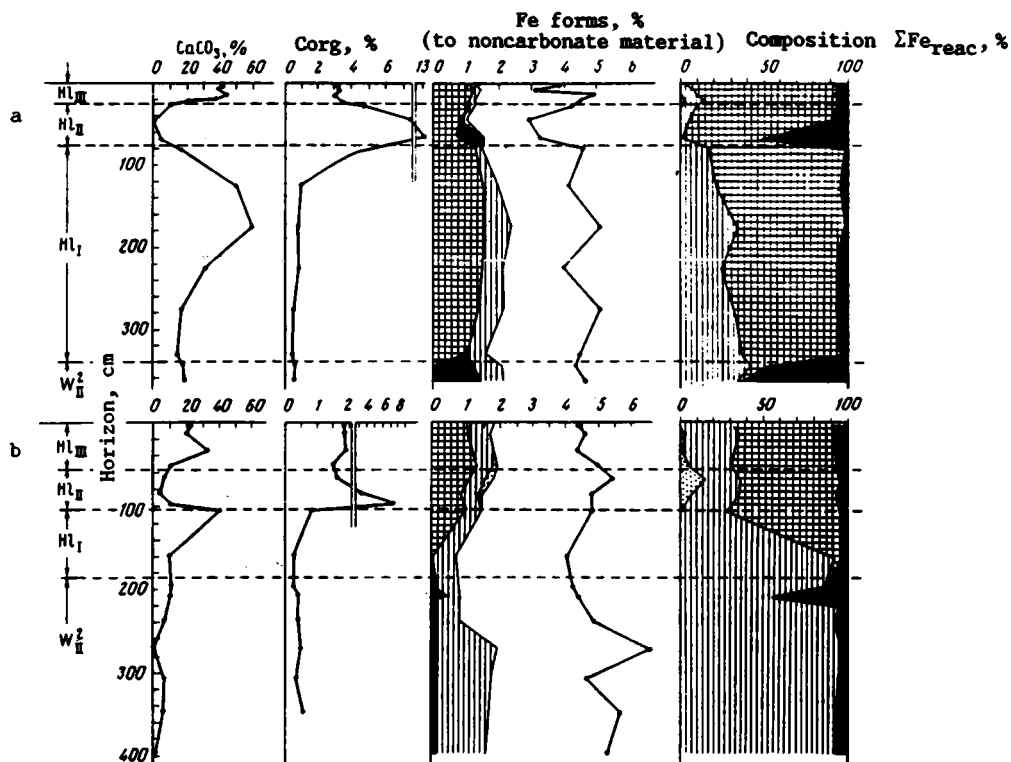


Fig. 4. Distribution of C_{org} , $CaCO_3$, and iron forms in deposits of the upper part of the western (st. 888) and northern (st. 792) slopes: a) st. 888, depth 570 m ($43^{\circ}42.1'$ N.lat., $30^{\circ}18.2'$ E.long.); b) st. 792, depth 602 m ($44^{\circ}38.1'$ N.lat., $32^{\circ}07.0'$ E.long.). Lensed as in Fig. 2.

Further changes in the content of components of the horizon upwards in the section are extremely varied for the different morphometric zones of the sea. In pelagic deposits (see Fig. 2a, b, st. 806, 840), insignificant changes in the C_{org} content are observed (0.3-0.5%), with small increase in carbonate (up to ~10%), and notable growth in Fe_{total} , without expressed tendencies of change in the total reactivity of the iron. The latter represent sulfide iron (Fe hydrotroilite) and nonsulfide Fe(II), which are present in comparable quantities, as well as an admixture of iron pyrite (2-3% of ΣFe_{reac}). In the sediments of st. 840 it is possible to note the presence of an inverse correlative connection (a variation of ~0.3%, see Fig. 2a) between sulfide and nonsulfide iron (or sulfide and ΣFe_{reac}). This connection is absent in sediments from the central part of the western chalistase (st. 806). Such indicators of correlation between total and reactive iron are absent from all of the hydrotroilite horizons.

In the slope sediments (see Fig. 3, st. 805, 852) with higher C_{org} , $CaCO_3$, and Fe_{total} contents relative to the pelagic zone, it is possible to note their marked increase in the upper hydrotroilite interbed immediately underlying the Holocene sediments. The increase of Fe_{total} in these interbeds is confirmed by the abrupt growth of reactive iron, which is almost entirely represented by iron hydrotroilite. At the same time, a minimum of Fe_{total} corresponds to the hydrotroilite interbed detected in the lower part of core of st. 805. This minimum corresponds to the extremely insignificant contaminant content of detrital iron forms (see Fig. 3a). This iron form relationship is detected in the lower part of the pelagic zone section of st. 806 (see Fig. 2b). It is noteworthy that in the investigated shelf sediments (see Fig. 5c, st. 795) the practical absence of detrital forms of iron corresponds to the upper hydrotroilite bed (horizon 300-310 cm).

In the section of a single hydrotroilite horizon from the upper part of the southern slope (see Fig. 5a, st. 829), the C_{org} and $CaCO_3$ content is practically unchanged, while the Fe_{total} decreases. In comparison with other middle Novoevksinsk deposits, these sediments are distinguished by a significantly greater pyrite content (up to ~10% of ΣFe_{reac}).

Late Novoevksinsk deposits ($H1_I$) are completely represented in all of the considered sections. As a rule, the onset of their accumulation agrees with a sharp reduction in hydro-

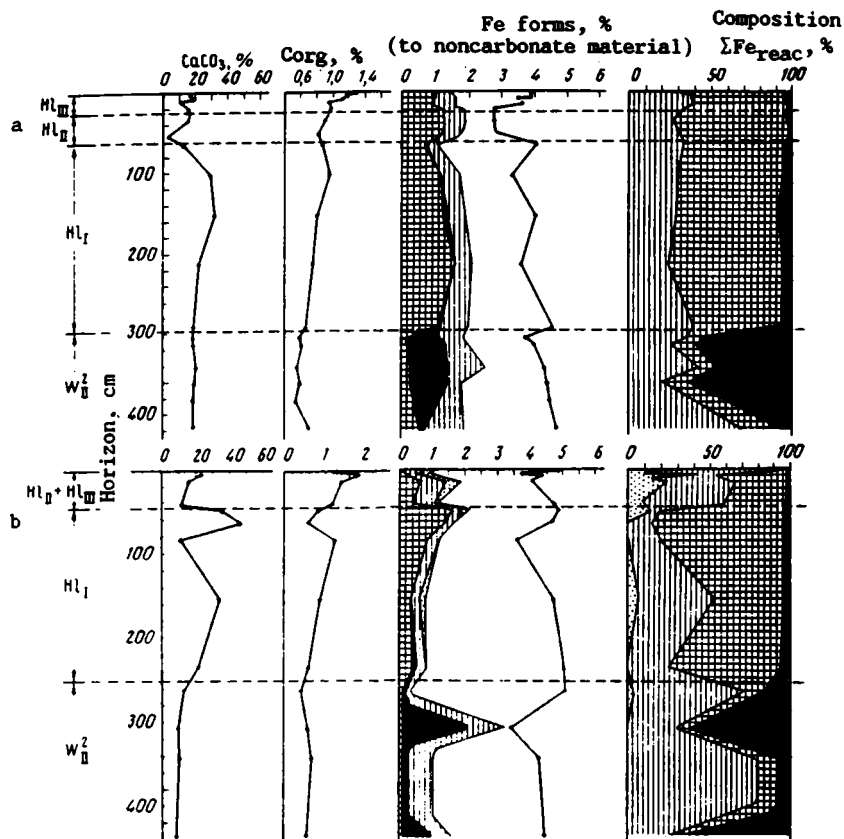


Fig. 5. Distribution of C_{org} , $CaCO_3$, and iron forms in deposits of the upper part of the Anatolian slope (st. 829) and Kalamitsk shelf of the Crimea (st. 795): a) st. 829, depth 240 m ($41^{\circ}57.5'$ N.lat., $35^{\circ}39.2'$ E.long.); b) st. 795, depth 150 m, ($44^{\circ}45.5'$ N.lat., $32^{\circ}51.3'$ E.long.). Legend as in Fig. 2.

troilite mineralization, although this is quite conditional. However hydrotroilite mineralization does not disappear completely, and it appears in the form of discreet, insignificant interbeds, lenses, gouge, and microdisseminations of acid-dissolved sulfides, which are in the general case distinguished by contaminant contents of S^{2-} , with a tendency to decrease upwards in the section. Sulfide mineralization in these sediments is mainly represented by highly dispersed disseminations of pyrite (see Figs. 2-5), whose particles, probably deprived of hydrotroilite pegmentation, are tinted to a light grey color. An underlying sapropel transition bed of sediment made up of clay-carbonate pelite and silty-pelite mud with a microlayered character is detected in the upper part of the horizon. Its thickness varies from 1 to 25 cm. Close to the base of the Ancient Black sea horizon, the Novoevksinsk sediments sometimes acquire green-brown tint. Discreet interbeds of silty carbonate material of 1-10 cm thickness, as well as crusts which are lithified by carbonate cement often occur in the limits of the horizon (st. 840). The thickness of the late Novoevksinsk deposits depends on the sea's morphometric zone and region. On the shelf and the upper part of the slope (with exclusion of st. 792, see Fig. 4b) it is significantly greater than in the pelagic zone and the lower part of the slope, while in the sediments of the eastern chalistase (see Fig. 2c, st. 839) it is higher than in the west (see Fig. 2b, st. 806). A dependence of the horizon thickness on the floor relief is noted: In level parts, the boundary with hydrotroilitic middle Novoevksinsk sediments lies deeper than in the sharply dissected areas.

In comparison with the underlying hydrotroilite sediments, the late Novoevksinsk deposits of the western part of the sea are characterized by a significantly higher content of C_{org} (to 0.8-1%) and $CaCO_3$ (to 10-20% in the pelagic zone and 40-60% on the slope), which overall increases upwards in the section, with noted variations in individual layers. In a series of cases of slope sediments (see Fig. 5a, st. 829 and Fig. 4a, st. 888), the growth of $CaCO_3$ content is succeeded by its decrease. In the shelf sediments (see Fig. 5b, st. 795), the distribution character of $CaCO_3$ is complicated by the high-carbonate interbeds ($CaCO_3$ up to 50%), underlying the Ancient Black Sea muds.

On the whole, the character of the distribution of reactive forms of iron in the section of Novoevksinsk deposits is not inconsistent with known geochemical and lithological data [1, 2, 4, 7]. At the same time, more frequent testing of cores may make it possible to refine and improve detail in the overall picture of the distribution of these forms. The following facts are most significant in the subsequent interpretation.

The hydrotroilite deposits are separated from the Ancient Black Sea deposits by a rather thick sequence of principally pyritized sediments, which, in agreement with the substratification, comprise the late Novoevksinsk (lower Holocene) horizon H₁ [4, 7, 8] (see Fig. 2-5). In the pelagic deposits, the sum of iron connected into sulfides (hydrotroilite + pyrite), is on average roughly the same both in the hydrotroilite, and in the late Novoevksinsk horizons (see Fig. 2).

Sulfide mineralization of slope and shelf sediments of the late Novoevksinsk horizon (see Figs. 3a, 5b) appears mainly in the form of individual hydrotroilite interbeds, divided by a significant sequence of sediments depleted in sulfides, or sometimes completely without sulfides [6, 9]. A complete range of the contaminant content of detrital forms of iron up to their complete absence, is observed (see Figs. 2b, 3a and 5b).

The lower boundary of the hydrotroilite horizon detected in the sediments of the slope foot from the northwest slope (see Fig. 2a, st. 840), is noted by the synchronous decrease in C_{org}, Fe_{total}, and CaCO₃ contents, as well as the increase in ΣFe_{reac} in the composition of Fe_{total}.

It is extremely significant that the late Novoevksinsk sediment of the investigated shelf region (see Fig. 5b, st. 795) contains notable quantity of nonsulfide reactive trivalent iron (to ~10% from ΣFe_{reac} in the middle part of the horizon, and up to 17% in the upper beds).

Individual interbeds, detected in the section of the pelagic zone of the late Novoevksinsk horizon, also draw attention. Sharp falls in the content of C_{org} accompanied by the characteristic alternation of pyrite and hydrotroilite mineralization are observed in them (see Fig. 2a, b; st. 840, horizon 140-160 cm; st. 806, horizon 100-130 cm).

Digressing from the numerous and varied individual effects of the distribution of the investigated components and estimating the average content of sulfide forms of iron and the thickness of corresponding horizons (see Figs. 2-5), it is possible to see that the overall accumulation of reduced sulfur in the Novoevksinsk deposits from a series of shelf and upper slope regions (see Figs. 4a and 5) is on the whole no less and sometimes notably greater than in the sediments of the pelagic zone.

ANCIENT BLACK SEA DEPOSITS

Sediments of the Ancient Black Sea horizon in the investigated sections demonstrate the practically complete spectrum of lithologic features described in the literature [4, 7]. In the pelagic zone and the lower part of the slope of the western part of the sea (see Figs. 2 and 3, st. 806, 840, 805, 852) they are extremely similar and are represented by homogeneous green-brown noncarbonate microlayered sapropelic muds. The horizon is characterized by sharp lithologic contacts with the underlying and overlying sediments, and comparatively increased moisture content (to 86%, st. 840). A so called marker horizon is detected as a rule in its upper part (5-7 cm from the cover). It is a fine (1-2 mm) clay-carbonate coccolithic interbed, extending to the limits of the entire deep water basin. The sapropelic muds with high contents of organic material often display special elastic properties. The thickness of the horizon varies within limits of 50-60 cm.

In comparison with the underlying late Novoevksinsk sediments, the deep water Ancient Black Sea deposits of the western are sharply depleted in calcium carbonate, with a maximum fall in CaCO₃ content on the lower boundary of the horizon coming from the lower part of the continental slope (see Fig. 3, st. 805, 852). On the whole, the distribution of C_{org} in the section bears an extreme character, in which the greatest increases in C_{org} contents are correlated to the middle parts of the horizon.

Sulfide mineralization is principally represented by pyrite, which is the main component of total reactive iron. However notable enrichment of relatively underlying sediment by acid dissolved sulfides, both in absolute content, and in the composition of ΣFe_{reac} is observed in individual beds. There is a series of individual differences in the distribution of forms

of Fe and S in sections of the horizon from each of the investigated cores. In the central part of the western chalistase (see Fig. 2b, st. 806), the maximum absolute pyrite contents correspond to the horizon boundaries, and the middle part, which is the richest in organic material, is depleted in FeS_2 . It is however, enriched in hydrotroilite (up to 20% $\text{FeSulfide of } \Sigma\text{Fe}_{\text{reac}}$). Significant changes in FeS_2 content are not observed on the lower boundary close to the slope foot (see Fig. 2a, st. 840); pyrite enrichment is found only on the upper boundary or the horizon. A sharp increase in the sulfidization of reactive iron is characteristic for both stations at the transition from late Novoevksinsk sediments to the sapropel sediments, however in the center of the khalistase this occurs due to the acid soluble sulfides (see Fig. 2). An increase of total sulfides, whose maximum however tends toward the middle part of the horizon, is also observed in sediments from the lower part of the slope. Its lower boundary demonstrates both a small increase of FeS_2 (see Fig. 3a, st. 805), as well as a minimal sulfide content (see Fig. 3b, st. 852).

Apart from the indicated differences it is necessary to note the presence of a specific interbed enriched by CaCO_3 (76%) in the central part of Ancient Black Sea horizon, at st. 840, which is absent in the sediments of all of the other stations. This interbed is a response to the maximum enrichment of sediment by organic material (C_{org} 17.2%). It contains woody fragments and other remnants of land vegetation. Its presence is not reflected in the distribution of forms of Fe in the composition of $\Sigma\text{Fe}_{\text{reac}}$, and in absolute contents, the non-carbonate material is recorded by a sharp maximum of these forms (see Fig. 2a).

In distinction from the monolithic muds of the western part of the sea, the Ancient Black Sea horizon in the center of the eastern chalistase (see Fig. 2a, st. 839) is expressed by a sequence of individual, thin, sapropel-like ($\text{C}_{\text{org}} \leq 5\%$), sometimes breccia-like, interbeds, with clay-silt, green-grey muds with variable CaCO_3 content (<22%). The minimal CaCO_3 content (~10%) clearly corresponds to the organogenic interbeds. The overall thickness of the horizon is notably higher than in the center of the western chalistase (85 cm at st. 839; 60 cm at st. 806). The lower sapropel-like interbed is distinctly marked by increase of both the absolute pyrite content, and by its fraction in $\Sigma\text{Fe}_{\text{reac}}$. However, these magnitudes are much smaller than in the sediments of the western stations. The upper interbeds (as well as the bottom of the horizon at st. 840, see Fig. 2a) demonstrate the increase in the sulfidization of Fe_{reac} , due to hydrotroilite. On the whole, the distribution of forms of Fe_{reac} are not significantly distinguished from those distributed in the underlying late Novoevksinsk horizon.

Notable differences appear in the Ancient Black Sea sediments from the upper part of slope in different regions of the sea. In deposits of the Anatolian slope from the eastern part of the sea (st. 829, depth 240 m) this horizon is practically indistinguishable by lithologic indicator. In this case, the late Novoevksinsk carbonate-clay muds, enriched by shells of *Dreisensia*, transform across an unclear boundary (similar to the adjacent sediments of the shelf) to silt-clay coccolithic and diatomic weakly calcareous sediments, which do not contain sapropels. As a result of chemical analyses (see Fig. 5a) the lower boundary of the horizon is clearly recorded by a sharp increase in the pyrite content and a fall in carbonate. It is apparently possible to identify the lithologically extremely conditional upper boundary with the decrease of FeS_2 and $\Sigma\text{Fe}_{\text{reac}}$, and the increase of Fe_{total} . Notice is paid to the fact that for the noted falls in the content of these components, in practice the onset and history of Ancient Black Sea sediment accumulation do not reflect the magnitudes of C_{org} and the fraction of Fe_{pyr} in $\Sigma\text{Fe}_{\text{reac}}$.

The Ancient Black Sea horizon is considerably better expressed in the upper part of the slope in the sea's western region. Both the lower and upper boundaries of the horizon are recorded rather distinctly in the lithology on an interval adjacent to the Kalamitsk Gulf (see Fig. 4d, st. 792, depth 602 m). The horizon is represented by typical sapropel-like, weakly carbonate, microlayered sediments. The lower boundary, denoted by the fall of carbonate and sharp increase in C_{org} is a response to the extremely insignificant alterations in Fe_{pyr} , $\Sigma\text{Fe}_{\text{reac}}$, and Fe_{total} . In addition, the distinctive sign of this transition is contained in the appearance of reactive trivalent iron, whose content increases upwards in the section, reaching 17% of $\Sigma\text{Fe}_{\text{reac}}$ in the upper part of horizon. The pyrite content also increases somewhat, while in this case this increase occurs during a significant decrease in the C_{org} content.

The Ancient Black Sea horizon is yet more clearly expressed in the upper part of the northwest slope (see Fig. 4a, st. 888, depth 570 m), with an outer form similar to deep water

sapropelites. In this region it is made up of biogenic and organogenic-detrital sapropel and sapropel-like muds, as well as of terrigenous noncarbonate and weakly carbonate sediments. In this case microlayering is absent, and brecciation of sapropel-like material and traces of slumping and redeposition of organogenic sediments is observed in a series of cores. The character of CaCO_3 and C_{org} distribution is close to that described for st. 792 (see Fig. 4b) (at a maximum on the lower boundary, decreasing upwards in the section), while the distribution of forms of Fe is practically identical to the horizon of deep water st. 840, close to the slope foot (see Fig. 2a).

In shelf deposits, with rare exception, the late Novoevksinsk muds form a rather distinct lithologic contact with the covering sediments, while there are extremely weak to practically absent outer lithologic differences between the Ancient Black Sea and Recent horizons. Examination of the st. 795 core (see Fig. 5b) from the lower part of the Kalamitsk Gulf shelf demonstrates the sharp reduction of the rather homogeneous "late Novoevksinsk" horizon (44 cm to the sediment surface) of clay-carbonate, green-grey mud without signs of stratification. The most noteworthy feature in the behavior of the investigated components lies in the fact that with the transition from the Novoevksinsk sediment to those of the Ancient Black Sea, apart from the decrease in CaCO_3 , there is a sharp drop in the pyrite content, the total sum of reactive iron, as well as Fe_{pyr} in the composition of $\Sigma\text{Fe}_{\text{reac}}$ for an insignificant increase of C_{org} . As in the underlying horizon, the sediments contain a notable quantity of $\text{Fe(III)}_{\text{reac}}$ (10-25% of $\Sigma\text{Fe}_{\text{reac}}$).

The discussed indicators of the investigated component distribution (see Figs. 2-5, horizon H_{III}) illustrate and actualize the rather well known overall representation of geochemical features in the sediments of the Ancient Black Sea horizon [4-7]. First of all, it is necessary relate them to the extremely uneven distribution of buried organic material (or remnant C_{org}) both between individual morphometric zones and geographic regions of the sea, and in the section of the horizon. Over the scale of the entire sea this unevenness is expressed in the C_{org} enrichment of sediments in the western part of the basin on the whole and of its western regions, also including the middle part of the slope (see Fig. 4a, st. 888). The differences between deep and shallow water deposition are particularly great. The sediments of the shelf and upper part of the slope are either completely deprived of sapropels, or contain isolated fine sapropel-like interbeds. The thickness of the Ancient Black Sea horizon in these zones as a rule is also reduced.

An extremely important circumstance is included in the presence of a significant quantity of nonsulfide reactive Fe(II) in the composition of $\Sigma\text{Fe}_{\text{reac}}$ (a maximum up to 40%, see Fig. 3a), disregarding the overall high degree of sulfidization [2]. At the same time, in individual fine beds of the Ancient Black Sea sediments, $\Sigma\text{Fe}_{\text{reac}}$ is practically completely represented by sulfide forms (see Figs. 2a, 3a, b).

The regularity in the distribution of sulfide mineralization in the Ancient Black Sea deposits by no means reflects the observed unevenness in the distribution of buried organic material (OM). The total content of iron sulfides (pyrite and hydrotroilite) in the section of the horizon averages ~1% and varies in limits 0.8-1.2% outside its dependence on abrupt variations in C_{org} . It is roughly the same both in sediments with relatively low contents of C_{org} (~1-2%), which principally comprise the Ancient Black Sea horizon on the shelf (see Fig. 5b), in the upper part of the slope (see Figs. 4b and 5a), and in the center of the eastern chalistase (see Fig. 2c), and in the sapropel muds of the western part of the sea, where the C_{org} content reaches 10-17% (see Figs. 2a, b, and 3). The average sulfide content is also rather similar in the sediments which are sharply distinguished by C_{org} content of the Ancient Black Sea and late Novoevksinsk horizons on the whole, although the Ancient Black Sea muds may be both enriched (see Figs. 2b, c and 3a) and depleted (see Figs. 3b and 5b) in sulfides relative to the underlying bed of Novoevksinsk sediments. As a rule, the Ancient Black Sea horizon of deepwater sediments in the western part of the sea is significantly depleted in sulfides in comparison with the covering Recent deposits, in which the C_{org} content is at the same time significantly less (see Figs. 2a, b and 3). In a series of cases, it is possible to observe an inverse connection between the distribution of sulfides and C_{org} in a section of the Ancient Black Sea horizon (see Figs. 2b and 3b).

The notable increase of sulfide content accompanying the growth of C_{org} is only observed on the lower boundary of the Ancient Black Sea horizon in sediments of the central parts of the chalistase (see Fig. 2b, c). However, it is evident that first of all it is a response to the increase of total iron content (Fe_{total}) at the expense of the reactive forms.

At the same, the rather notable variability (0.8-1.2%) in the content of sulfide forms of iron in a section of the horizon, observed on a background of nearly average contents in the sediments from different sea zones, makes it possible to state the existence of definite genetic connections between the sulfide forms, the sum of Fe_{reac} and Fe_{total} , expressed in the correlation of the corresponding magnitudes. It is necessary to note that the obtained data for each section are clearly insufficient for quantitative estimation of the degree of correlation, however there is no doubt in a qualitative treatment of correlation on the level of colinearity of distribution curves.

The direct connection between Fe_{total} and ΣFe_{reac} is most clearly apparent in the deep water deposits of the western part of the sea (see Figs. 2a, b and 3). It is much weaker in the pelagic zone of the eastern part (see Fig. 2c), and it is absent in the upper part of the slope and on the shelf (see Figs. 4 and 5a, b), or it transforms to an inverse connection.

The relation of sulfide forms of Fe in deep water sediments is also rather variable, however a positive connection between F_{pyr} and ΣFe_{reac} is evident for the noted sharp predominance of pyrite over hydrotroilite. The increased degree of sulfidization in individual interbeds is realized by this, as a rule, due to the acid soluble sulfides (see Figs. 2a, 3 and 4a).

RECENT DEPOSITS (Hl_{III})

The Recent (late Holocene) horizon in sediments of the western part of the sea, both in the pelagic zone, and in different regions of the slope, is represented by clay-carbonate (coccolithic) and terrigenous weakly carbonate muds with clearly expressed alternation of coccolithic (light grey), clay (green), and sapropel (dark) microlayers. It is characteristic that such microlayering (not inherent to the shelf sediments) begins to appear at depths greater than 250 m. In the pelagic zone the horizon thickness comes to 25-30 cm, and it is reduced on the slope (10-20 cm). These deposits contain on average 3.5-4.5% C_{org} , however conversion to noncarbonate material indicates that the absolute C_{org} content in individual organogenic interbeds is rather great (8-12%) and similar to the C_{org} contents in the Ancient Black Sea weakly carbonate sediments. For the transition from sapropels to Recent deposits in the deep water regions of the western part of the sea, the sharp fall in the C_{org} content is accompanied by an increase in Fe_{reac} , an increase in the degree of its sulfidization due to pyrite (up to 95%), and a reduction in the hydrotroilite component (see Figs. 2a, b and 3). These changes are less definitely expressed in the sediments of the upper part of the slope and shelf (see Fig. 4) or contradictory tendencies are observed (see Fig. 5a). Further alteration in the contents of the components upwards in the section may have a different character, however in the deepwater sediments there remains an overall appearance of a direct correlative connection between the Fe_{total} , ΣFe_{reac} , and F_{pyr} noted for the Ancient Black Sea horizon. For sufficient thicknesses of the horizon and test frequency (e.g., st. 806, 840), it is possible to observe a unique rhythm in the distribution of C_{org} , as well as pyrite and correspondingly in ΣFe_{reac} and Fe_{total} . With this, C_{org} and FeS_2 are often altered opposite phases of one another (see Fig. 2). The detection of trace quantities of reactive Fe(III) in Recent sediments of the pelagic zone (st. 806) is extremely interesting (2-3% of Fe_{reac} , see Fig. 2b).

Two subhorizons are distinguished by geochemical data in Recent deposits of the central region of the eastern chalistase (see Fig. 2c, st. 839). In the lower, made up of homogeneous, green-grey, carbonate-clay mud (~60 cm), the contents of the components are practically the same as in the Ancient Black Sea deposits (with exception of C_{org}) and late Novoevksinsk sediments. In the upper part (15-20 cm to the surface) analogous to the western stations, sharp decreases of $CaCO_3$, C_{org} , FeS_2 are observed, and the characteristic rhythm of their distribution in fine beds begins to appear.

The behavior of the investigated components in the surface layers of Recent deposits of the sea's oxygen and hydrogen sulfide zones is sharply distinguished (see Fig. 2 and 5b). This reflects the differences in the character of diagenetic processes occurring at the present time.

Considering the combination of discussed observations, it is not difficult to be convinced that the distribution of the investigated forms of Fe and S (along with the distribution of C_{org} , $CaCO_3$, and lithologic characteristics) reflect both the sequential alternation

of stratigraphic horizons, that is, the evolution of sediment formation conditions, and the specifics of these conditions in individual morphometric zones and geographic regions of the sea. They may be utilized for the reconstruction of the overall pathway of the late Quaternary sedimentary process. Clarification of the formation conditions for the complex of reactive forms of iron, and most of all of sulfides is a necessary premise of such reconstruction. On the basis of the discussed actual material, and the results of the series of foregoing investigations, the author will try to consider a possible pathway for these processes in the subsequent report.

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The mineralogical and chemical composition of Mn-microconcretions has been studied in various pelagic deposits in the northern Equatorial Pacific. Microconcretions form essentially during the early diagenetic stage near the bottom sediment-water interface. The chemical composition and diagenetic transformation of sediments have practically no influence on the chemical makeup of microconcretions. In certain sediment types microconcretions represent the main source of Mn and Ni.

Important problems in microconcretion studies include the question of source of the ore matter, means of migration and mechanical deposition of the main MC components. In the following, we review data on the chemical and mineral composition of microconcretions, as well as their interrelationships with pelagic deposits in the north Equatorial Pacific region.

The studied microconcretions (MC) were extracted from sediments, sampled during the 28th and 41st Cruises of R/V Dmitrii Mendeleev [6, 8, 11, 14]. Microconcretions >0.05 mm in size, were extracted under binocular microscope, along with the undisturbed enclosing sediments from the same horizon [4]. The samples were studied by bulk analysis, using the atomic absorption method. The twelve elements analyzed include: Al, Fe, Mn, Ti, K, Ni, Co, Cu, Zn, Cr, Pb, Li. Ca and V were analyzed only in MC. The calculated concentration coefficient (k_m) of the elements in the microconcretions and the impact of the sediment chemistry (C_m) provided the following formula:

$$C_m = M \cdot K_m,$$

where M is the ratio between the microconcretion and dry-sediment volumes.

The studied samples were Pliocene-Pleistocene limey and siliceous-clayey muds, miopelagic clays and Oligocene-Pliocene clayey-siliceous deposits, eu- and miopelagic clays. The Mn/Fe ratio in sediments varied from very small values to 3.54. The mean value was 0.31 (Table 1). The maximum value at Station #3834 [14] occurred where zeolitic-clayey sediments accumulated visible concentrations of Mn-microconcretions. These sediments were enriched not only in Mn but also in Ni, Cu, Zn. These sediments generally display low concentrations of Ti, Ni, Co, Cu, Zn, Cr and Pb. At an average Al concentrations of 5.29%, the Al content increases in siliceous-clayey muds and eupelagic clays. The Fe content generally increases in mio- and eupelagic clays. The mean K content was 2.16%. Relative Li enrichment occurs in clayey-radiolarian muds and zeolitic-clay deposits.

The Mn-microconcretions differ in their very varied chemical composition (Table 2) and wide range of mineral phases [3, 4, 19, 24, 34, etc.]. Sediments, in particular in the north equatorial Pacific (Stations #2474-27, 2483-36 and 2492) contained the following Mn minerals: vernadite, todorokite, asbolane, mixed-layer asbolane-buserite, Na and Ca-birnessite. A 10 Å buserite-like mineral, absent in earlier studies, and Ni-birnessite also occurred. The iron minerals included hydrogoethite and feroxyhyte. All these 10 Å-Mn minerals occurred mostly in the Pleistocene deposits. Their quantities steadily declined in transition toward the Pliocene sediments (mixed-layer asbolane-buserite was the main 10 Å-mineral form) and are totally absent from Oligocene and Miocene deposits. A reverse relationship exists between abundance of the 7 Å-Mn-phase and decreasing sediment ages. The degree of birnessite crystallization gradually increases and reaches a maximum in Oligocene deposits. Gradual replacement of the 10 Å-Mn minerals by 7 Å-Mn minerals apparently indicates their diagenetic alteration throughout geologic time.

In the MC, the mean Mn/Fe ratios vary between 2.4-72.0 (Table 2). This mean value was 15.7, with a range of 1.7-61.1, in the studied samples. The maximum came from Oligocene radiolarian muds. High MC values are typical of Pleistocene miopelagic clays, low ones, of

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TABLE 1. Chemical Composition of Microconcretion-Bearing Deposits*

Station number	Horizon, cm	Sediment type	Al	Fe	Mn	Ti	K	Ni	Co	Cu	Zn	Cr	Pb	Li	Mn/Fe
3830-13	0-9	PPDR + PPCR	6.70	4.36	0.28	-	3.13	0.015	0.006	0.059	0.018	-	156	10 ¹¹	0.06
3830-18	2-5	PPCR	5.50	4.27	0.42	-	2.68	0.015	0.001	0.039	0.011	-	83	84	0.10
3830-41	5-8	OPRC	4.43	3.65	1.49	-	1.96	0.094	0.005	0.050	0.017	-	84	65	0.41
3830-42	3-6	OPMC	6.87	5.10	0.80	-	2.76	0.049	0.005	0.011	0.024	-	110	88	0.16
3833-1	0-2	PPDR	7.61	5.50	0.43	-	2.20	0.017	0.005	0.035	0.015	-	134	58	0.08
3833-13	4-20	OPMC	4.09	7.76	3.06	-	1.80	0.081	0.008	0.108	0.023	-	96	64	0.39
3833-27	1-2	PPDR	5.58	4.57	0.16	-	-	0.014	0.006	0.037	-	-	-	-	0.03
	2-3	"	6.22	4.38	0.30	-	-	0.014	0.006	0.035	-	-	-	-	0.07
	3-4	"	-	4.34	0.30	-	-	0.013	0.005	0.035	-	-	-	-	0.07
	4-5	"	5.42	4.61	0.30	-	-	0.015	0.007	0.034	-	-	-	-	0.06
	8-14	PPCR	6.18	5.39	0.30	-	-	0.014	0.006	0.034	0.009	-	-	-	0.05
3833-35	175-180	PPMC	-	8.38	0.15	-	-	0.009	0.006	0.034	0.015	-	-	-	0.02
	248-254	"	-	9.81	0.02	-	-	0.004	0.004	0.037	0.015	-	-	-	0.00
	355-360	OPEC	-	10.09	1.27	-	-	0.028	0.016	0.069	0.020	-	-	-	0.13
3834	55-60	OPZC	4.90	4.07	14.4	0.27	1.87	0.521	0.013	0.435	0.078	23	45	111	3.54
	65-70	"	5.76	5.60	5.13	0.34	2.03	0.221	0.010	0.205	0.050	19	35	69	0.92
	88-95	OPMC	4.40	6.36	2.89	0.26	1.71	0.122	0.006	0.130	0.029	8	22	59	0.45
	155-161	"	3.48	6.33	1.24	0.20	1.44	0.041	0.004	0.070	0.019	3	30	53	0.20
2474-13	5-10	PPCR	6.42	5.00	0.36	0.35	-	0.012	0.007	0.029	0.015	82	60	-	0.07
2474-27	340-345	OPRM	2.15	1.89	0.42	0.07	-	0.009	0.002	0.021	0.010	32	48	-	0.22
2483-36	230-235	OPMC	5.91	4.56	1.34	0.24	-	0.033	0.006	0.061	0.022	54	72	-	0.29
2492	120-125	OPEC	5.90	5.10	1.02	0.32	-	0.030	0.011	0.056	0.018	71	68	-	0.20
	350-355	OPZC	6.92	5.34	1.08	0.31	-	0.024	0.007	0.040	0.017	46	64	-	0.20
2512-2	0-5	PPDR	6.61	4.80	0.48	0.29	-	0.013	0.006	0.030	0.015	135	56	-	0.10
2520-10	13-18	PPFC	2.31	1.27	0.12	0.09	-	0.004	0.001	0.029	0.005	28	60	-	0.09
2520-11	3-8	"	3.17	1.92	0.19	0.14	-	0.005	0.002	0.021	0.009	89	68	-	0.10
Mean values for each sediment category															
		PPFC	2.74	1.60	0.16	0.12	-	0.005	0.002	0.025	0.007	59	64	-	0.10
		PPDR	6.29	4.70	0.33	0.29	2.20	0.014	0.006	0.034	0.015	135	135	58	0.07
		PPCR	6.20	4.76	0.34	0.35	2.91	0.014	0.005	0.040	0.013	82	100	92	0.07
		OPRC	4.43	3.65	1.49	-	1.96	0.094	0.005	0.050	0.017	-	84	65	0.41
		OPRM	2.15	1.89	0.42	0.07	-	0.009	0.002	0.021	0.010	32	48	-	0.22
		PPMC	-	9.10	0.09	-	-	0.007	0.005	0.036	0.015	-	-	-	0.01
		OPEC	5.90	7.60	1.15	0.32	-	0.029	0.014	0.063	0.019	71	68	-	0.17
		OPZC	5.86	5.00	6.87	0.31	1.95	0.255	0.010	0.227	0.048	29	48	90	1.55
		PPMC	4.95	6.02	1.87	0.23	1.92	0.065	0.006	0.076	0.023	22	66	66	0.30
Mean sedi- ment values			5.29	5.17	1.45	0.24	2.16	0.054	0.005	0.067	0.021	49	76	75	0.31

*Cr, Li and Pb content in 10⁻⁴ percentages; rest: in percentages.

**Pliocene-Pleistocene categories: PPCR) clayey-radiolarian mud; PPDR) diatom-rich miopelagic clay; PPRC) radiolarian-clayey; PPFC) foraminifer-coccolitic mud; PPCM) miopelagic lay. Oligocene-Pliocene categories: OPRM) radiolarin mud; OPRC) same, radiolarin-clayey; OPEC) eupelagic clay; OPZC) zeolite clay; OPZ) zeolite; OPMC) miopelagic clay. Analyses by N. N. Zavadskaya and V. V. Gordeev.

TABLE 2. Mean Element Composition of Microconcretions from the Northern Equatorial Pacific Zone, %

Number of samples	Mn	Fe	Ni	Cu	Co	Zn	Mn/Fe	References
—	50,5	0,7	0,30	0,40	—	—	72,0	[25]
22	39,5	3,8	1,42	1,47	—	—	10,4	[23, 36]
23	26,1	3,6	1,16	0,81	0,14	0,22	7,2	[29]
120	35,0	3,1	1,60	1,20	—	—	11,3	[23, 28]
2*	29,2	2,1	1,45	0,64	0,27	—	13,9	[32]
71	41,2	1,03	0,52	0,03	—	—	40,0	[26]
9	23,9	5,1	0,73	0,99	0,17	0,15	4,7	[33]
6	20,2	8,4	0,94	0,67	0,15	—	2,4	[20]
35	23,3	5,8	1,28	0,74	0,23	—	4,0	[35]
64	30,3	2,9	1,16	1,00	0,18	0,16	15,7	Present paper

*Mean values, based on 31 microprobe measurements.

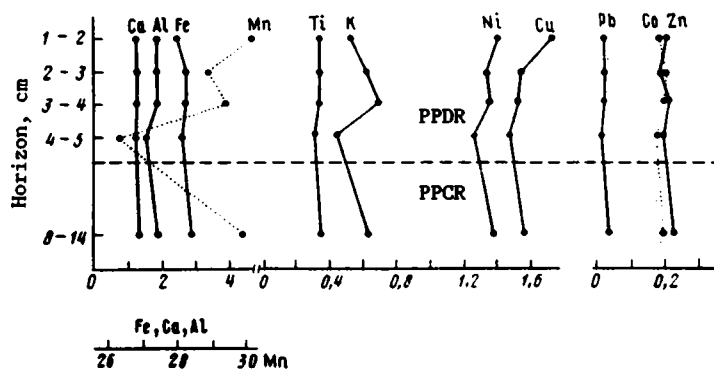


Fig. 1. Interrelationships between basic components, Station #3833-27%, %.

foraminifer-coccolithic muds (Table 3). Chemical composition of MC generally also changes somewhat with the type of enclosing sediments, reflecting an interrelationship with the depositional conditions. Thus, MC in the diatom-enriched, clayey-radiolarian muds differ in their maximum Cu concentration and increased mean Fe, Co, Zn and Cr content. The clayey-radiolarian muds MC are enriched in Li and contain relatively large quantities of Cu, Zn, Cr and Pb. Against a background of increased Li and Cu content, the maximum Ca and Zn values occur in MC of clayey radiolarian muds. Heavy enrichment of Fe, Cr, Co and Ti and Ni depletion occur in MC in foraminifer-coccolithic muds. Old radiolarian muds contain MC of minimal Al, Fe, Co, Cu, Zn and Ti content, but are strongly enriched in Mn. Minimum Cr, lowered Al, V, Ca and Co content and relative Mn-enrichment is typical of MC in old clayey-radiolarian sediments. MC in Pleistocene miopelagic clays are depleted in Fe, Ni, Zn and Cr, but greatly enriched in Mn, V, T, Co and Pb. Significant Fe, Ca and Zn enrichment occurred in MC, found in old miopelagic clays. In the eupelagic clay group (including zeolitic-clayey sediments and zeolites), the Mn/Fe ratios and the Mn, V and Cr content in the MC gradually declines with increasing zeolite content in the deposits. The Al content showed a reverse trend. A high Pb and Co content characterized MC from eupelagic clays.

The MC composition varied greatly, depending on the size of the analyzed fractions (Table 3). With decreasing MC-size, Mn, Co, Zn and Pb increased statistically, while the Al, K, Cr, Ca and Li content decreased. The Fe, Ti, V, Ni and Cu content behaved ambiguously. Figures 1-4 indicates the relationships between elements in the entire >0.05 mm MC fraction.

Clayey-radiolarian muds (Fig. 1) were dredged at Station #3833-27. The upper part of the section was diatom-enriched. A greatly-reduced Mn content was noted in the MC at the boundary between the two sediment types. This trend was much weaker for K, Ni, Cu and Co. The Ca, Al, Fe, Ti, Pb and Zn content down the core displayed insignificant variability. Positive correlations were noted between the Mn and Ni, Cu contents.

TABLE 3. Chemical Composition of Mn-Microconcretions*

Station number	Horizon, cm	Size fraction, mm	Sediment type**	Al	Fe	Mn	Ti	K	V	Ca	Ni	Co	Cu	Zn	Cr	Li	Pb	Mn/Fe
3830-13	0-9	> 0.5	PPDR + PPCR	1.67	1.73	34.20	0.18	0.54	0.027	1.38	1.07	0.17	1.43	0.253	15	322	220	19.8
3830-18	2-5	0.1-0.25	PPCR	0.1	2.99	22.41	0.03	0.42	0.015	1.51	1.11	0.14	1.12	0.232	53	286	500	7.5
3830-41	5-8	> 0.25	OPRC	1.14	1.72	32.68	0.52	0.75	0.026	0.87	1.05	0.09	0.84	0.124	7	115	230	19.0
		0.1-0.25	"	1.31	1.97	32.88	0.30	0.66	0.031	0.93	1.04	0.09	1.11	0.138	12	96	220	16.7
3830-42	2-6	0.1-0.25	OPMC	1.01	1.83	31.10	0.26	0.87	0.037	1.24	1.52	0.24	0.87	0.143	27	150	260	17.0
	0-8	> 0.25	PPDR + ODMC	2.89	3.19	23.29	0.44	0.60	0.037	1.23	1.01	0.18	1.27	0.145	28	181	160	7.3
		0.1-0.25	"	2.26	2.36	26.82	0.51	0.60	0.038	1.24	0.99	0.15	1.20	0.160	13	150	230	11.4
3833-1	0-2	> 0.25	PPDR	1.95	2.81	31.79	0.39	0.52	0.034	1.49	1.39	0.20	1.59	0.210	15	133	330	11.3
3833-4	5-9	> 0.25	PPCR	1.82	2.53	30.38	0.35	0.51	0.031	1.41	1.41	0.18	1.60	0.206	20	126	330	12.0
3833-13	4-20	0.5-1.0	OPMC	3.26	4.78	20.23	0.46	0.77	0.035	0.93	0.76	0.15	0.64	0.065	16	78	230	6.2
		0.25-0.5	"	1.73	4.95	25.60	0.48	0.58	0.041	1.19	1.14	0.12	0.69	0.105	12	59	340	5.2
3833-27	1-2	> 0.1	PPDR	1.85	2.42	30.17	0.34	0.52	0.035	1.26	1.41	0.19	1.73	0.203	26	163	190	12.5
	2-3	> 0.1	"	1.83	2.73	28.91	0.34	0.61	0.036	1.28	1.34	0.20	1.54	0.192	33	140	190	10.6
	3-4	> 0.1	"	1.86	2.70	29.41	0.34	0.70	0.032	1.30	1.36	0.20	1.53	0.195	19	157	150	10.9
	4-5	> 0.1	"	1.59	2.56	26.27	0.32	0.45	0.031	1.24	1.26	0.18	1.47	0.187	29	127	70	10.3
	8-14	> 0.1	PPCR	1.86	2.84	29.93	0.35	0.63	0.034	1.33	1.37	0.19	1.58	0.219	36	150	270	10.5
3833-35	175-180	> 0.1	PPMC	3.10	2.89	25.77	1.43	0.86	0.037	0.80	0.87	0.85	0.94	0.050	29	125	710	8.9
	248-254	> 0.25	"	1.48	0.89	35.32	0.12	0.60	0.026	0.84	0.98	0.20	0.68	0.154	10	605	180	39.7
	355-360	> 0.1	OPEC	1.38	1.65	37.06	0.52	1.06	0.064	0.78	0.78	0.33	0.69	0.097	9	47	490	22.5
	380-385	> 0.1	"	1.39	1.80	35.89	0.44	1.06	0.053	0.87	1.12	0.26	0.74	0.124	12	46	360	19.9
3911-48	2-5	0.1-0.25	PPCR	2.26	3.41	23.98	0.49	0.71	0.030	1.37	1.37	0.19	1.06	0.120	15	80	290	7.0
	5-10	0.1-0.25	"	2.65	3.16	22.97	0.44	0.67	0.028	1.25	1.20	0.17	0.93	0.116	17	92	230	7.3
3911-76	0-7	> 0.25	PPDR + PPCR	1.95	2.37	29.32	0.30	0.54	0.032	1.68	1.28	0.16	1.44	0.265	16	154	340	12.4
3911-83	0-3	> 0.25	PPDR	2.03	3.24	30.37	0.34	0.54	0.036	1.69	1.15	0.23	1.54	0.206	23	148	380	9.4

TABLE 3 (continued)

Station number	Horizon, cm	Size fractions, mm	Sediment type ¹⁰	Al	Fe	Mn	Ti	K	V	Ca	Ni	Co	Cu	Zn	Cr	Li	Pb	Mn/Fe
3834	3-6	> 0.25	"	2.19	3.58	28.56	0.49	0.56	0.039	2.08	1.11	0.21	1.46	0.186	25	124	420	8.0
	55-60	0.5-1.0	OP2C	1.50	1.19	35.21	0.13	0.68	0.028	1.18	1.19	0.028	1.02	0.157	10	164	50	29.6
		0.25-0.5	"	1.76	1.56	33.55	0.15	0.72	0.033	1.15	1.15	0.043	1.04	0.157	12	146	80	21.5
	60-65	0.1-0.25	"	2.06	1.82	33.23	0.16	0.66	0.034	1.11	1.12	0.059	1.10	0.155	14	138	80	18.3
	65-70	> 0.25	"	1.58	1.50	33.23	0.15	0.83	0.032	1.24	1.33	0.032	1.00	0.189	10	138	80	22.2
3905	80-88	> 0.25	"	1.48	1.70	32.99	0.18	0.76	0.031	1.26	1.31	0.044	1.07	0.208	10	116	110	19.4
	88-95	> 0.25	"	1.83	2.64	30.79	0.32	0.64	0.040	2.93	1.15	0.070	1.30	0.210	16	114	140	11.7
	155-161	> 0.25	OPMC	1.24	4.12	32.20	0.46	0.58	0.047	1.52	1.08	0.068	1.19	0.184	14	95	200	7.8
		> 0.05	"	0.81	5.62	30.20	0.63	0.52	0.047	4.10	0.77	0.082	0.78	0.169	8	87	260	5.4
	0-5	> 0.1	PPDR	0.87	5.29	25.64	0.03	0.53	0.051	1.63	1.16	0.067	1.58	0.227	72	219	300	4.8
	120-125	0.1-0.25	PPMC	2.27	2.32	22.84	0.79	0.80	0.028	1.12	0.81	1.64	0.42	0.091	24	113	1030	9.8
	225-230	> 0.1	"	1.20	0.85	38.79	0.40	0.50	0.041	0.97	0.65	0.39	0.89	0.064	21	97	1950	45.6
	295-300	> 0.25	"	1.30	0.92	40.57	0.21	0.83	0.055	0.88	0.39	0.055	0.95	0.063	20	63	90	44.1
		0.1-0.25	"	1.16	0.83	40.22	0.24	0.82	0.047	0.85	0.38	0.065	0.79	0.071	8	53	110	48.5
	300-305	> 0.25	"	1.29	0.97	38.40	0.20	0.79	0.051	0.91	0.39	0.048	0.89	0.073	11	68	90	39.6
3915		0.1-0.25	"	1.21	0.83	39.08	0.25	0.98	0.044	0.88	0.41	0.064	0.72	0.077	10	64	120	47.1
	340-345	> 0.25	"	1.97	1.93	32.87	0.38	0.65	0.047	1.36	1.38	0.11	1.15	0.124	15	100	280	17.0
	0-8	> 0.05	PPDR + PPCR	1.74	2.32	31.65	0.32	0.59	0.039	1.54	1.08	0.19	1.29	0.226	13	274	320	13.6
3921	8-15	> 0.05	PPRC	1.71	2.45	29.30	0.32	0.40	0.036	1.67	1.12	0.16	1.41	0.221	15	161	320	12.0
	0-5	> 0.5	PPCR + PPCR	2.22	2.85	29.16	0.33	0.58	0.033	1.81	1.25	0.15	1.44	0.233	22	160	280	10.2
3923		0.25-0.5	"	1.94	2.59	28.94	0.28	0.55	0.034	1.93	1.30	0.15	1.27	0.207	13	132	310	11.2
		< 0.25	"	2.12	3.70	29.35	0.31	0.57	0.044	1.81	1.31	0.17	1.49	0.221	25	128	200	7.9
	215-220	> 0.25	OPZ	2.88	2.17	26.24	0.29	1.06	0.023	1.23	1.56	0.073	0.75	0.159	15	99	90	12.1
		0.1-0.25	"	2.45	2.23	27.44	0.29	1.15	0.024	1.24	1.53	0.125	0.64	0.171	13	86	130	12.3
	220-230	> 0.25	"	2.89	2.30	24.94	0.30	1.24	0.024	1.45	1.40	0.078	0.63	0.156	11	83	110	10.8
		0.1-0.25	"	2.51	2.33	27.38	0.31	1.19	0.026	1.23	1.40	0.102	0.63	0.177	12	80	130	11.8
	260-265	> 0.25	"	3.44	2.50	26.77	0.34	1.33	0.024	1.38	1.39	0.058	0.67	0.187	21	112	140	10.7
		0.1-0.25	"	2.71	2.44	27.95	0.33	1.20	0.022	1.26	1.37	0.076	0.76	0.194	18	97	120	11.5
	265-275	> 0.25	"	2.81	2.52	24.97	0.32	1.25	0.024	1.43	1.31	0.052	0.63	0.155	13	86	110	9.9
		0.1-0.25	"	2.56	2.53	25.92	0.30	1.22	0.024	1.40	1.37	0.077	0.70	0.165	11	84	120	10.2
285-290		> 0.25	OPZC	3.23	2.58	27.91	0.33	1.26	0.025	1.32	1.54	0.061	0.74	0.190	19	114	120	10.8
		0.1-0.25	"	2.67	2.30	29.24	0.32	1.30	0.027	1.27	1.53	0.082	0.70	0.198	16	99	130	12.7

TABLE 3 (continued)

2520-10	13-18	> 0,05	PPFC	3.26	14,69	25,60	1,30	-	-	-	0,54	0,40	0,65	0,14	180	-	800	1,7
2520-11	3-8	> 0,05	"	2,07	11,07	23,20	0,86	-	-	-	0,31	0,30	0,61	0,08	690	-	700	2,1
2512-2	0-5	> 0,05	PPDR	1,81	4,50	26,20	0,38	-	-	-	0,55	0,11	0,90	0,09	360	-	300	5,8
2474-13	5-10	> 0,05	PPCR	1,81	4,48	29,00	0,56	-	-	-	0,65	0,24	0,83	0,08	430	-	600	6,5
2474-27	340-345	> 0,05	OPRM	0,56	0,66	40,30	0,26	-	-	-	0,96	0,03	0,16	0,09	50	-	200	61,1
2483-36	230-235	> 0,05	OPMC	1,26	1,90	43,50	0,23	-	-	-	2,17	0,15	0,30	0,15	210	-	200	22,9
2492	120-125	> 0,05	OPEC	1,60	3,10	32,80	0,46	-	-	-	2,01	0,31	0,64	0,09	60	-	300	10,6
	350-355	> 0,05	OPZC	2,81	3,21	35,60	0,25	-	-	-	2,81	0,17	0,56	0,11	30	-	200	11,1
Mean values for each sediment category																		
			PPDR	1,82	3,32	28,59	0,33	0,55	0,037	1,50	1,19	0,198	1,49	0,187	67	151	259	9,3
			PPFC	2,67	12,88	24,40	1,08	-	-	-	0,43	0,350	0,63	0,110	435	-	-	1,9
			OPEC	1,77	2,87	28,21	0,34	0,58	0,030	1,43	1,17	0,181	1,26	0,191	68	186	348	10,8
			PPRC	1,98	2,89	29,19	0,31	0,53	0,037	1,81	1,25	0,158	1,40	0,221	19	170	278	10,3
			OPRC	1,23	1,85	32,78	0,41	0,71	0,029	0,90	1,05	0,091	0,98	0,131	9	106	225	17,9
			OPRM	0,56	0,66	40,30	0,26	-	-	-	0,96	0,030	0,16	0,090	50	-	200	61,1
			PPMC	1,66	1,38	34,87	0,45	0,76	0,042	0,96	0,70	0,379	0,83	0,085	16	143	507	33,4
			OPEC	1,46	2,18	35,25	0,47	1,06	0,059	0,83	1,30	0,300	0,69	0,104	27	47	383	17,7
			OPZC	2,10	2,05	32,30	0,22	0,86	0,031	1,43	1,45	0,065	0,95	0,175	15	129	110	17,5
			OPZ	2,78	2,38	26,45	0,31	1,21	0,024	1,33	1,42	0,080	0,68	0,171	14	91	119	11,2
Mean sediment values			OPMC	1,81	3,60	29,12	0,43	0,65	0,040	1,64	1,18	0,142	0,87	0,140	41	114	235	10,4
				1,93	2,85	30,27	0,39	0,76	0,028	1,36	1,16	0,178	1,00	0,156	47	134	284	15,7

*Cr, Li and Pb content in 10^{-4} percentages, other elements: in percentages.

**See notes to Table 1.

Analysis by N. N. Zavadskaya and G. I. Sychkova.

TABLE 4. Concentration Coefficients (Km) of Elements in Microconcretions

Station number	Horizon, cm	Sediment type*	Al	Fe	Mn	Ti	K	Ni	Co	Cu	Zn	Cr	Pb	Li
3830-13	0-9	PPDR +PPCR	0,25	0,41	122,1	-	0,17	71,3	27,0	24,4	13,8	-	1,4	3,2
3830-18	2-5	PPCR	-	0,70	53,4	-	0,16	75,0	100,0	29,1	21,1	-	6,0	3,4
3830-41	5-8	OPRC	0,28	0,51	22,0	-	0,36	11,2	20,2	19,6	7,6	-	2,7	1,6
3830-42	3-6	OPMC	0,15	0,36	38,9	-	0,32	31,2	45,3	82,9	5,9	-	2,4	1,7
3833-1	0-2	PPDR	0,26	0,51	73,9	-	0,24	80,8	38,5	45,3	14,0	-	2,5	2,3
3833-13	4-20	OPMC	0,61	0,63	7,5	-	0,38	11,8	17,3	6,2	3,8	-	3,0	1,1
3833-27	1-2	PPDR	0,33	0,53	194,6	-	-	100,7	29,7	47,3	-	-	-	-
	2-3	"	0,29	0,62	97,3	-	-	93,1	32,8	44,4	-	-	-	-
	3-4	"	-	0,62	98,0	-	-	103,8	37,7	44,1	-	-	-	-
	4-5	"	0,29	0,56	88,5	-	-	82,4	26,5	43,4	-	-	-	-
	8-14	PPCR	0,30	0,53	101,5	-	-	101,5	33,9	45,9	25,2	-	-	-
3833-35	175-180	PPMC	-	0,34	174,1	-	-	100,0	-	27,8	3,3	-	-	-
	248-254	"	-	0,09	1766,5	-	-	233,3	46,5	18,2	9,9	-	-	-
	355-360	OPEC	-	0,16	29,2	-	-	27,8	20,1	10,0	4,8	-	-	-
3834	55-60	OPZC	0,36	0,37	2,4	0,56	0,37	2,2	3,3	2,4	2,0	0,52	1,6	1,3
	65-70	"	0,26	0,30	6,4	0,53	0,37	5,9	4,6	5,2	4,1	0,53	4,0	1,7
	88-95	OPMC	0,28	0,65	11,1	1,77	0,34	8,9	12,1	9,2	6,3	1,75	11,8	1,5
	155-161	"	0,23	0,89	24,3	3,15	0,36	18,9	19,5	11,1	9,0	2,67	16,0	0,6
2474-13	5-10	PPCR	0,28	0,97	80,6	1,60	-	55,6	33,8	28,6	5,2	5,3	9,8	-
2474-27	340-345	OPRM	0,47	0,35	96,0	3,71	-	106,7	20,0	7,5	9,0	1,7	3,8	-
2483-36	230-235	OPMC	0,21	0,42	103,6	0,96	-	66,8	25,0	5,0	6,8	4,0	2,4	-
2492	120-125	OPEC	0,27	0,61	32,2	1,44	-	67,4	29,5	11,4	5,3	0,9	4,7	-
	350-355	OPZC	0,41	0,60	33,0	0,81	-	115,2	23,9	14,2	6,6	0,6	2,5	-
2512-2	0-5	PPDR	0,27	0,94	54,6	1,31	-	78,7	17,2	30,0	6,1	2,6	6,1	-
2520-10	13-18	PPFC	1,41	11,57	213,3	14,40	-	154,3	363,6	53,3	26,5	6,50	13,0	-
2520-11	3-8	"	0,65	5,77	122,1	6,14	-	57,4	150,0	29,3	8,5	7,74	10,0	-
Mean value of sediment category														
		OPRC	0,28	0,51	22,0	-	0,36	11,2	20,2	19,6	7,7	-	2,7	1,6
		OPRM	0,47	0,35	96,0	3,71	-	106,7	20,0	7,5	9,0	1,7	3,8	-
		PPCR	0,28	0,65	89,4	1,60	0,17	75,9	48,7	32,0	16,3	5,3	5,7	3,3
		PPDR	0,29	0,63	101,2	1,31	0,24	89,9	30,4	42,4	10,1	2,6	4,3	2,3
		PPMC	-	0,22	970,3	-	-	166,7	46,5	23,0	6,6	-	-	-
		OPMC	0,30	0,59	37,1	1,96	0,35	27,5	23,8	22,9	6,4	2,8	7,1	1,2
		OPEC	0,27	0,39	30,7	1,44	-	47,6	24,8	10,7	5,1	0,9	4,7	-
		OPZC	0,34	0,42	13,9	0,63	0,37	41,1	10,6	7,3	4,2	0,55	2,7	1,5
		PPFC	1,03	8,67	167,7	10,27	-	105,9	256,8	41,3	17,5	7,12	11,5	-
Mean micro-concretion value			0,37	1,15	140,3	3,03	0,31	71,6	47,1	26,8	9,3	2,90	5,8	1,8
Mean macroconcentration values [1]			0,5	3,3	60,0	2,6	0,5	66,0	41,0	19,0	9,0	0,5	22,0	1,7

*See note to Table 1.

TABLE 5. Impact of Chemical Composition of the >0.05 mm-Microconcretion Category on the Sediment Chemistry, C_m , %

Station number	Horizon, cm	Sediment type*	Al	Fe	Mn	Ti	Ni	Co	Cu	Zn	Cr	Pb	M, %
2474-13	5-10	PPCR	0,01	0,03	2,66	0,05	1,83	1,12	0,94	0,17	0,17	0,32	0,033
2474-27	340-345	OPRM	0,06	0,08	23,03	0,89	25,60	4,80	1,79	2,17	0,41	0,91	0,240
2483-36	230-235	OPMC	0,02	0,04	2,82	0,08	5,81	2,18	0,43	0,59	0,34	0,21	0,087
2492	120-125	OPEC	0,04	0,08	4,18	0,19	8,77	3,84	1,48	0,68	0,12	0,61	0,130
	350-355	OPZC	0,18	0,26	14,17	0,35	49,52	10,30	6,10	2,82	0,26	1,08	0,430
2512-2	0-5	PPDR	0,01	0,02	1,09	0,03	0,87	0,34	0,60	0,12	0,05	0,12	0,020
2520-10	13-18	PPFC	0,04	0,34	6,19	0,42	4,47	10,55	1,55	0,77	0,19	0,38	0,029
2520-11	3-8	"	0,02	0,14	2,93	0,15	1,38	3,60	0,70	0,21	0,19	0,24	0,024
3834	55-60	OPZC	5,87	6,03	39,12	9,13	35,86	53,79	39,12	32,60	8,48	26,08	16,30
	65-70	"	2,62	3,03	64,58	5,35	59,53	46,41	52,47	41,37	5,35	40,36	10,09

*See note to Table 1.

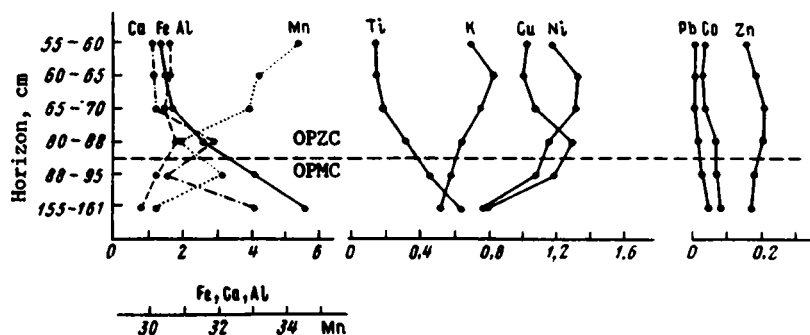


Fig. 2. Interrelationships between basic components, Station #3834, %.

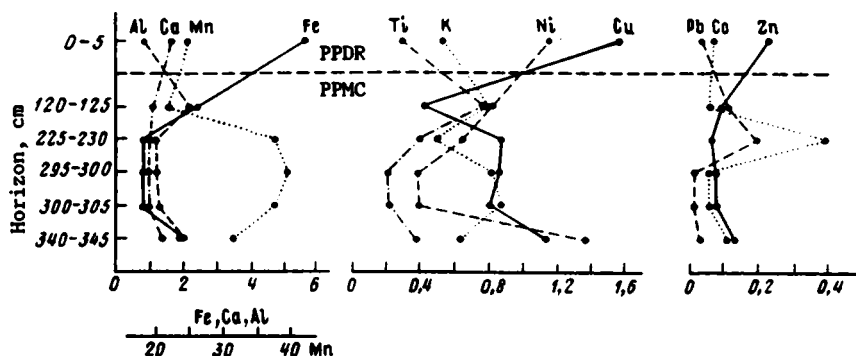


Fig. 3. Interrelationships between basic components, Station #3905, %.

MC were studied from zeolitic-clayey sediments and old (Oligocene-Pliocene) miopelagic clays at Station #3834 (Fig. 2). The Pb, Fe, Ti and Co content gradually increased in the MC near this section, while the Al content declined. The other elements displayed more complex behavior. Reverse graphic correlation existed between Mn and Ca. The Ni vs. Zn and K, and Fe vs. Ti-distribution patterns showed identical trends.

The core at Station #3905 contained Pliocene-Pleistocene miopelagic clays (Fig. 3), covered by a thin, diatom-rich, clayey radiolarian mud layer. The MC content varied greatly in relation to their position in the section. Below horizon 120-150 cm, the Mn, Cu content increased unevenly in the MC. The Al, Fe and Ti content decreased. The Ca and Zn content was quite uniform, while K, Ni, Co and Pb contents were characterized by significant fluctuations. Clearcut correlations were absent between the elements.

Microconcretions from Station #3923 (Fig. 4) were derived from zeolitic-clayey sediments and zeolites. Independently of the sediment category, the Ca, Fe, Ti, Pb and Co content of the microconcretions remained very similar in all samples. Small variations occurred in the concentrations. Cu, Zn and Ni displayed slight correlation with Mn. Al correlated directly with Mn.

Comparison of MC chemical composition with that of the sediments (Tables 1 and 3) indicated no strong correlations. Mn, Fe, Ni, Cu, Co and Zn MC-concentration plots (Fig. 5) in a given sediment type occasionally were distributed in a fairly narrow field in the diagrams. An overall plot of MC values from various sediment types displayed no recognizable distribution trend for any element in the microconcretion-sediment system.

The chemical composition of the MC thus correlated only poorly and ambiguously with the composition and age of the enclosing sediments. The MC, therefore, did not inherit the chemical composition of the sediments during diagenesis. The relationship between analyzed elements in MC frequently is a random one. Apparently, it is essentially related to a combination of variable depositional factors at the moments of microconcretion formation, near the bottom sediment-water interface. Mn, the main microconcretion component is the most sensitive indicator of the variability of conditions during sediment accumulation.

The elements behavior during MC formation provides the coefficient of microconcretion concentrations (K_m) in the microconcretions (Table 4). The K_m values apparently are controlled by the chemical characteristics of the elements. Two element groups were identified

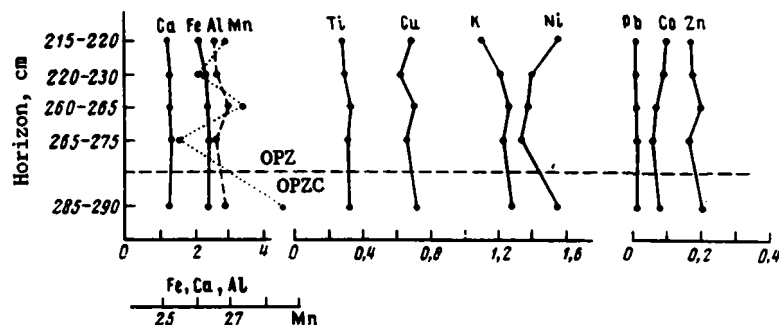


Fig. 4. Interrelationships between basic components, Station #3923, %.

in terms of their ability to concentrate [6]. Ni, Mn, Co, Cu, Zn and Pb represent the first group. Their mean K_m values are greater than 5. Cr, Ti, Sr, Ba and Fe were depleted in the second group. Their mean K_m values ranged between 1.3-2.5. Al was separate from this group; its mean concentration coefficient, ~ 0.3 .

The earlier observed patterns were also recognized in the studied samples (Table 4). In comparison with the sediments, the MC were generally depleted in K, Al and Fe. Microconcretions from the foraminifer-coccolith muds are an exception. The mean K_{Al} value approaches 1 and the K_{Fe} value was 8.67 in these muds. Their microconcretion composition probably was influenced by the dissolution of limey muds near the critical compensation depth. Freed clay particles are captured by the growing microconcretions and their Al, Fe, Mn, Ti, Co and other element compositions increase. A very minor Li, Cr, Ti, Zn and Pb-enrichment of the MC has been observed. The K_m values for these elements are one-to-two magnitudes greater than for Mn, Ni, Co and Cu. The K_{Mn} and K_{Ni} maxima are typical of MC in Pleistocene miopelagic clays. The K_{Fe} , K_{Ti} , K_{Cr} , K_{Cu} , K_{Zn} , K_{Co} , and K_{Pb} values are highest in foraminifer-coccolith muds. High K_{Cu} values were found in MC of the clayey radiolarian muds, enriched in diatoms and in foraminifer-coccolith muds. The mean K_m values in the geochemical mobility series of the analyzed elements during MC formation show the following sequence: $Mn > Ni > Co > Cu > Zn > Pb > Ti > Cr > Li > Fe > Al > K$.

Comparison of mean concentration coefficient values in micro- and macroconcretions (Table 4) indicated that Mn, Ni, Co, Cr, Cu concentrate more intensively, and Fe and Pb less intensively in MC than they do in macroconcretions. Zn, Ti and Al behave in the same manner.

Evaluation of the impact of MC on the chemical composition of sediments (C_m) is shown in Table 5. Microconcretions (M) represent 0.002-16.3% of the dry sediments. The anomalously high M and C_m values are shown in the zeolite-clay sediments in Station 3834. This section has been previously described. Minor amounts of Al, Fe, Ti and Cr are typical of MC. If Station #3834 is excluded from consideration, then the greatest C_{Mn} content in MC (23.03%) occurs in old, radiolarian-bearing deposits. An increase in C_{Ni} values was also found in zeolitic-clayey deposits. These deposits differ from the in their maximum C_m values of Cu, Zn, Cr, and Pb. The C_{Co} values range between 0.34-10.55%. Minimum values occurred in clayey, diatom-rich radiolarian muds. High values were found in foraminifer-coccolithic muds and zeolitic-clayey deposits. Judging from the C_m distribution (Station #3834) endogenic sediment sources may influence MC formation.

The contribution of MC to the chemical composition of sediments is clearly minor: Microconcretions of size 0.05 mm and greater were used during analysis. The MC composition was not determined by separating ore and nonore (core) fractions. Unavoidable losses occurred during sample elutriation and MC separation from the sandy-silty sediment fractions. It was thought [22] that as much as 85% of the Mn from the sediments may be associated with MC. According to this assumption, the source sediment consisted of three components: microconcretions, clayey adsorbate, and clayey residue matter, insoluble in the Chester reagent. Strakhov [17] called these fractions nodular, hydrogenic (chemogenic) and lithogenic. The first two components represent the authigenic phase [17], while the clayey adsorbate consists of very fine MC.

MC contain the main forms of Mn in certain pelagic sediment types. This is partly also true of Ni that displays a positive correlation with Mn. Minor fractions of Ni and Mn probably also occur in noncrystallized colloidal Fe and Mn-hydroxides, oxidized films on altered

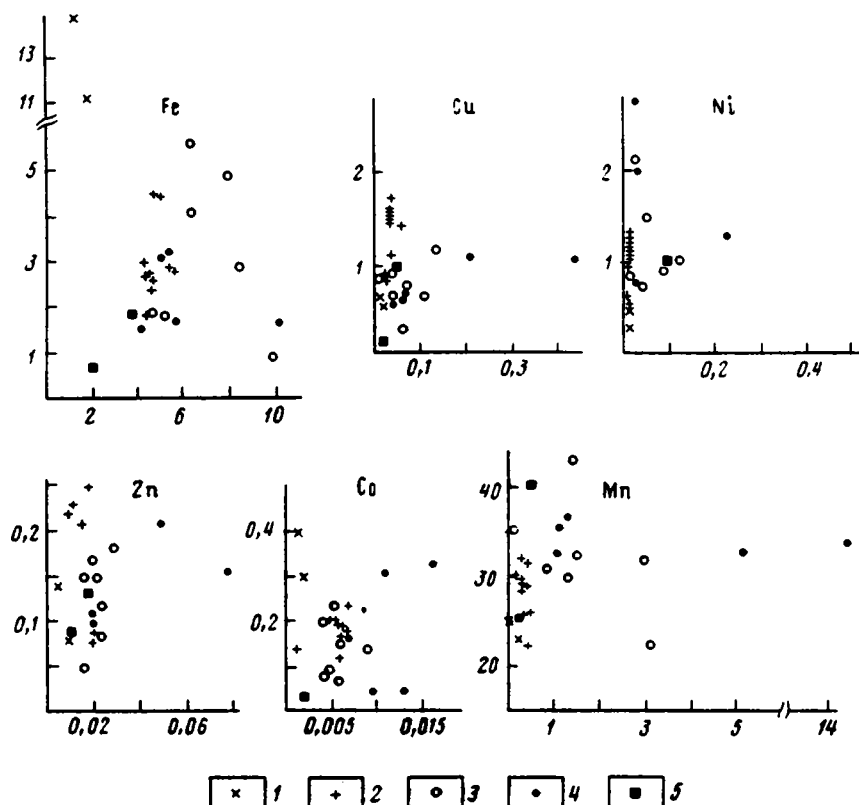


Fig. 5. Relationship between certain ore elements in sediments (abscissa; x-coordinate) and microconcretions (ordinate; y-coordinate), %. 1, 2) Pleistocene muds (1, foraminifer-rich-coccolithic; 2, clayey-radiolarian); 3-5) Oligocene-Pleistocene deposits (3, Pleistocene and Miocene miopelagic clays; 4, eupelagic clay, zeolite-clay deposits, zeolite; 5, radiolarian-clayey and clayey-radiolarian deposits).

radiolarian surfaces [31]. Even smaller amounts occur on detrital minerals. Co, Cu and, to a lesser extent Zn, settles apparently at the same time as Mn and Ni do. The introduction of the other analyzed elements into MC happens quite accidentally and depends essentially on the composition of the nucleus, the fine lithogenic admixtures and on characteristics of the lithodynamic conditions on the bottom.

Traditionally, Mn-microconcretions have been related to diagenetic conditions. It was noted [30] that they are dissolved after burial, thus partly aiding macroconcretion growth. In Strakhov's most detailed lithogenic syntheses [15], analyzed in-depth by Logvinenko [5] and Vassoevich [2], water-saturated, loose sediments form during the sediment-forming phase. Physicochemically, they are unbalanced in numerous directions. Sediment diagenesis or sediment conversion into rocks essentially is also a physicochemical balancing process of a complex and multicomponent system of reaction-capable substances, influenced by thermodynamic conditions in the crust. When describing oceanic sediment lithogenesis, Strakhov [16, p. 5] stated that "The very low sedimentation rate in the pelagic realm and the highly oxidized sediment type generated a most peculiar course for postdepositional processes. Unlike reduced sediments in regular water basins and marginal zones of oceans, this course can not be described by stages. The early diagenetic stage is indistinguishable from the diagenetic stage of the late, or even early katagenesis; the stages are fused together." Even the final stage of sediment genesis, development of highly water-saturated sediments, is still incompletely defined in the scheme of pelagic oceanic sediment formation [16].

Based on the various sediment-forming factors and direct observations [10, 12, 13], the following lithogenic sequence is assumed to operate in pelagic areas: (1) sediment genesis phase, with the presediment genesis, protosyngenetic and syngenetic stages; (2) the diagenetic phase that also includes three stages, the protodiagenetic, early diagenetic, and late diagenesis. Stage subdivisions of subsequent rock alterations also follow Strakhov's scheme [15]. Mobilization, transport and pelagic deposition of source matter occurs during the

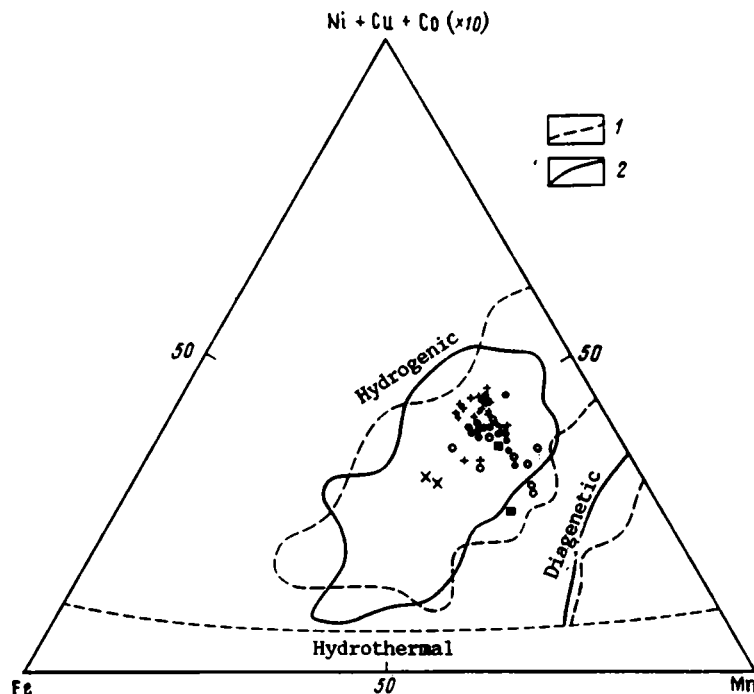


Fig. 6. Element interrelationship in studied microconcretions. 1, 2) microconcretion fields of various formation conditions [35]; macroconcretions [21]. For other provisional designations, note Fig. 5.

presedimentary stage. In 1922, Fersman defined syngeneses as mineral formation during sediment deposition; one of the initial lithogenic stages. It is the sediment-forming stage that precedes sediment diagenesis. Fersman later [18] regarded syngeneses (soil formation in basins) as a combination of biochemical, chemical, mineralogical and geophysical processes that leads to accumulation of specific time-stratigraphic lithosomes (marine muds, deposits, etc.) on the bottom of lakes, swamps, oceans and seas at the interface between lithosphere and hydrosphere.

According to Rukhin [9], syngeneses (halmyrolysis in the sense of K. Hummel) occurs during sediment settling in the highest sediment level. In certain instances, the sediments are colloidal, gel-like masses that contain more water than mineral matter. Syngenetic processes, with the exception of subaerial sediments, therefore occur in the presence of sufficient amounts of water and (with the exception of basins the bottom waters of which lack free oxygen), oxygen. The thickness of syngenetic zones, characterized primarily by oxidizing of neutral media, generally is less than 10-15 cm. Syngenetic processes are accompanied by vigorous bacterial activity.

In sorting out ideas by Fersman and Rukhin on syngeneses under pelagic depositional conditions, we have identified [10, 12, 13] protogenesis and syngeneses proper. A dense, ~1 cm thick suspension layer forms during protogenesis at the sediment-water interface. It passes into a thin (1-3 mm) layer of oxidized fluid mud with 90-95% water content. This ephemeral sediment layer is easily destroyed by bottom currents and its remnants carried downslope. However, under favorable conditions, the layers may lose their water content and thicken. During the syngenetic stage, 2-10 cm thick, semifluid, homogeneous, oxidized mud layers form. Homogenized layers form through intensive reworking of muds by small benthic organisms. The muds' water content ranges between 80-90%.

The **protodiagenetic stage** is characterized by underlying soft, oxidized beds, maximum 15 cm thick. Their water content ranges between 75-80%. The light-brown background color is complicated by quite rare cinnamon-brown and dark-brown round mottles, passages of burrowing organisms, filled by overlying sediments. Yellowish-brown mottles occur locally, outlining such features. Occasionally, dendritic Fe and Mn-hydroxide concentrates form, due to local element redistribution in a weakly-reducing medium.

Deposits, typical of the early diagenetic stage are usually found lower in the section. The beds here are 10-20 cm thick; they had been oxidized to varying degrees, somewhat compacted, and contain 70-75% water. Sharp color contrasts occur, reflecting completion of early diagenetic element reorganization in microenvironments of the reducing medium. Migration, primarily of Mn, as well as biological activity in the peripheral zone by benthic organisms led to local bleaching of sediments. The late diagenetic stage is the longest and "dullest" episode in the history of pelagic lithogenesis. Generally, gradual sediment compaction occurred downward in the section, accompanied by decreasing water content and porosity. Anaerobic bacterial activity diminished and nonbiogenic mobilization of matter started to predominate. The authigenic mineral structures became transformed through dissolution and redistribution of biogenic components that led to local sediment compaction; formation of silica concretions and nodules.

Formation of Mn microconcretions in pelagic sediments during diagenesis is denied by the following facts [14]: (1) Ore nodules occur in the bottom waters and in the surface film of the liquid sediment; (2) MC are distributed quite irregularly in each area of a uniform sediment type; (3) strong trends indicate decrease or increase in the amount of MC downward in each section, composed of a uniform sediment type; (4) during MC diagenesis, water is lost and the sediments become more compact. The structural ordering of Mn minerals increases [3]; (5) the amount of MC sharply increases during breaks in deposition; (6) a direct correlation exists between MC chemistry and the enclosing sediments; (7) the size of MC within a single sample showed considerable variations; (8) reducing processes that occur locally in pelagic sediments do not completely insure remobilization of ore components, required for MC formation; (9) the most favorable MC formation conditions existed at the water-sediment interface. These include: oxidizing conditions, sufficient amount of reacting organic matter, mixing of sediment matter by benthic organisms and bottom currents, introduction of ore elements from water layers, and diagenetic flux.

Based on this information, the manganese MC are considered chemogenic-syngenetic in origin. They formed essentially through colloid chemical processes near the water-bottom sediment interface. The theoretical foundations of these processes, supported by qualitative experiments, have been described by Morozov [7]. These are the main means for attaching colloidal Fe- and Mn-hydroxide particles to hard surfaces, composed of the reduced forms of these elements. Morozov considered the presence of dispersed particles, concretions, varied nuclei and particles on the bottom, including very minor quantities of Mn(II) and Fe(II) reduced forms, as the main precondition for the attachment of MnO_2 and $Fe(OH)_3$ to macro- and microconcretions. Mn(II) is fixed on such surfaces mainly through sorption from marine or muddy waters. Bivalent iron may enter the rock composition by entering minerals of concretion nuclei, also clay particles, and become stabilized during their decomposition in oxidizing media as multivalent compounds. Reduced forms of Mn and Fe may also develop on ore concretion surfaces through reducing microbiological processes.

Plotting of microconcretion data on a triangular diagram [21], indicated (Fig. 6) that the data points occur in the hydrogenic (not-diagenetic) distribution field and conform well with other research results [35].

* * *

The study of the distribution, mineral and chemical composition of Mn microconcretions in pelagic oceanic sediments indicated their ability to reflect depositional conditions very well. In their composition and distribution patterns the microconcretions that formed at the bottom-water interface reflect the original characteristics of the medium and are practically independent of ore element behavior in the sediment layer during early diagenesis. A sharp increase in the abundance or concentration of microconcretions in the section, represented by a single sediment type, serves as a dependable indicator of reduced sedimentation rates and breaks in deposition. Iron-enriched microconcretions (Fe-Mn-microconcretions) form near the critical carbonate accumulation (compensation) depth. Mn is the dominant ore component in the carbonate-free sediments. Ni, Co, Cu and Zn precipitate with Mn. During diagenesis, microconcretions may be partially dissolved or, at favorable locations, develop an ore-coating. Their basic changes involve improved crystallochemical ordering through transition from the 10 Å Mn structural phase to the 7 Å phase.

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The distinctive characteristics of sediments formed in polar seas which result from the influence of low temperatures (including temperatures below freezing point), and from the influence of ice on the depositional process have been summarized. Compositional features of Arctic marine sediments are described, together with the chemistry of their diagenesis and their authigenic mineralogy (by analysis of the composition and structure of early diagenetic concretions). The part played by cryogenesis in the lithogenesis of sediments in polar seas is shown.

Polar seas and oceans are the final destination of sedimentary material which is derived from an adjacent frozen landmass. The material is transported, either in solid form or in solution, by rivers, the wind, or glaciers, or is introduced by coastal erosion. In order to illustrate this, Table 1 compares the sources of sedimentary material in the Arctic Ocean with those in the world ocean as a whole. According to present estimates [11 and others], out of 25 billion tons of material transported from the land, the great majority (around 21.5 billion tons) is carried by rivers, 1.5 billion tons by the wind, and the same amount by glaciers and icebergs. Coastal erosion is thought to make the lowest contribution (0.5 billion tons) of sedimentary material to the sea.

The situation in polar seas is completely different. In the seas surrounding Antarctica almost all of the terrigenous material is carried from the land by glaciers and icebergs, and only a small proportion results from shore ice and the wind. Leont'ev [10] has calculated the sources of sedimentary material in the Arctic Ocean. According to the accepted method, the total amount of solid material being transported in all rivers into the ocean is taken to be twice the amount draining from the major rivers. For the 11 largest rivers entering the Arctic Ocean the total is estimated as 100 million tons/year. This is approximately equal to two rivers like the Tigris and Euphrates, and is five times less than the amount of solid material carried by the Mississippi alone into the Gulf of Mexico. Therefore, the total amount of solid material being drained into the Arctic Ocean equals 0.2 billion tons/year. This is approximately equivalent to the amount contributed by ice floes (0.18 billion tons/year). The majority of solid material, according to Leont'ev, is derived from the thermal-abrasive erosion of the coasts of the Arctic seas. This contributes around 1 billion tons/year, which is twice the figure provided by Lisitsyn [11] for the world ocean as a whole. Aeolian processes undoubtedly play a significant role in the transport of sedimentary material, although this is difficult to estimate due to the limited data [3]. The fact that terrigenous material is transported into the depositional basin by winds is demonstrated by the presence of windborne dust on floating ice at a great distance from the shore, and the development on the ice of aeolian relief forms.

Therefore, of the order of 1.4 billion tons/year of terrigenous material is carried from the land into the Arctic Ocean. Furthermore, it has been calculated that around 0.05 million tons is derived in suspension from the adjacent Pacific and, especially, Atlantic oceans. Biogenic material accounts for about 0.04 million tons/year. In other words, the amount of solid sedimentary material entering the Arctic basin each year totals about 1.5 billion tons, of which two thirds results from coastal erosion. This particularly affects coasts composed of easily erodable frozen rocks with a high content of ice. As the data above on the main sources of sedimentary material show, this situation is completely different from that in the world ocean as a whole, where more than 85% of material is transported in rivers.

Due to the cold water in the polar basins, most of the material in solution is transported into the adjacent oceans rather than being precipitated on the sea bed. Suspended and entrained particles are mostly deposited on the continental shelf, the maximum width of which (1300 km) is the greatest in the world. Only a relatively small proportion of the

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TABLE 1. Annual Supply of Sedimentary Material to the World and Arctic Oceans, billion tons/year (from [10, 11])

Source of sediment	World Ocean	Arctic Ocean
Rivers	21,55	0,2
Aeolian transport	1,6	?
Glaciers, icebergs, shore ice	1,5	0,18
Abrasion and thermal-abrasion	0,5	1,0
Volcanogenic material	2-3	?
Biogenic material	1,82	0,04
Material in suspension from adjacent oceans (for the Arctic Ocean)		0,05
Total	~30	1,47

terrigenous particles reach the deep-water parts of the ocean. Ice floes complicate the pattern of sediment distribution by distributing both fine-grained and coarse fragmental material to all of the regions where they drift. Ice plays an enormous part in the transport of sediment in polar seas. Each year ice floes cover a total area of the order of 26 million km² of seas and oceans, not including the areas covered by individual icebergs. That is about 7% of the total area of the world ocean [15]. Ice floes can be subdivided into fully marine shore and drift types, which may be annual or perennial (pack ice), and also types which are carried out to sea from rivers and glaciers (icebergs). After breaking away from the shore, shore ice also becomes drift ice. Shore ice and icebergs are of particular significance in terms of their ability to transport material [3, 5, 11]. Clastic material enters shore ice from several sources: from steep coast lines (by collapse, from scree, landslips and solifluction deposits), from shallow nearshore parts of basins where the ice rests on the sea bed and sediments become frozen within it, and large blocks and boulders may be squeezed out along fractures onto its surface. A distinctive feature of the lithic material transported by shore ice is its substantial content of material derived from the littoral and beach zones, which is typically well-rounded. As the shore ice moves along the beach, boulders with a characteristic shape are formed. They are truncated and striated on their upper surface and have a convex base, giving them a plano-convex shape. The lower, convex, surface of the boulder is buried within the beach sediment, and in the winter they are frozen together. In the spring the shore ice breaks off and begins to move, thus truncating the upper surface. A similar process takes place along the banks of the major rivers of Siberia during the spring ice movements, particularly at the site of ice jams where the ice moves over the boulder-covered banks. According to Zubova, the width of the zone of shore ice in the Arctic seas reaches 300-500 km, but is substantially less in the pre-Arctic seas, reaching about 25-50 km at the end of the winter (varying from 2 to 90 km) and with a thickness of 2 m.

Shore ice, in addition to supplying a large quantity of clastic material to the polar seas, also has the effect of preserving the development of lithodynamic processes. For about 9-10 months of the year wave activity, which is the main geological influence in marine coastal zones, does not occur. Furthermore, in the remaining 2-3 months, the drift ice limits wave development. Stable masses of floating ice, constantly added to by pack ice from central parts of the Arctic basin (Taimyr, Aion, Chukchi), never completely break up in the summer but only retreat northwards. As a result the shallow seas of the east Asian sector (Laptev, East Siberian), which reach depths of only 20-30 m over a wide area (i.e., subject to wave activity in other areas of the world ocean), accumulate fine-grained silty and argillaceous muds.

Ice within the Arctic basin drifts mainly towards the northwest, from the Chukchi and East Siberian seas, across the pole, towards eastern Greenland. In the part of the basin adjacent to North America the ice drifts in a closed circle due to the Coriolis force. Drift ice in the seas around the Antarctic also has a closed circumpolar character. The ice here is subject to abrupt seasonal variations: In winter it covers up to 19 million km² of the water surface, exceeding the area of the Antarctic landmass itself (around 14 million km²), whereas in summer (January-February) it reduces to a total of up to 2-3 million km². The width of the area of drift ice is greatest in the western hemisphere, where it reaches ~2000 km.

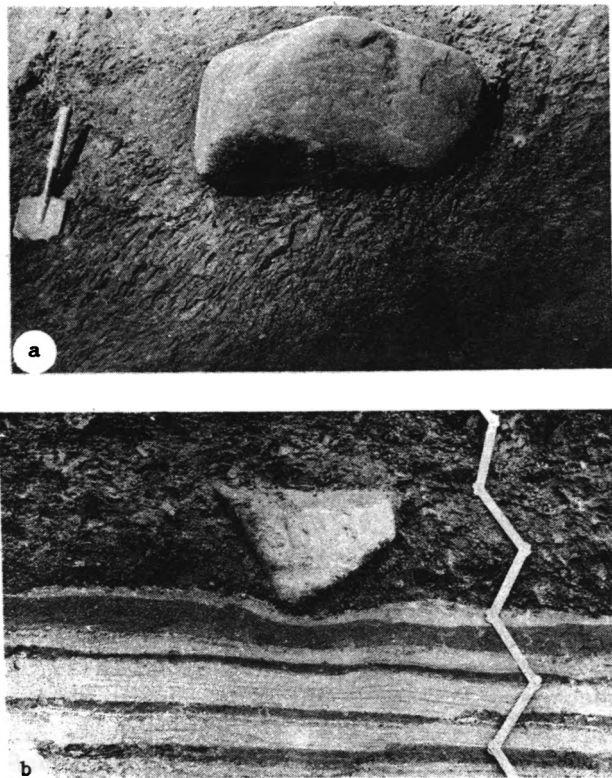


Fig. 1. Glaciomarine (cryomarine) deposits. a) Diamicton; unbedded, poorly sorted rock of a mixed psammitic, silty, and pelitic composition with isolated boulders and remains of a marine molluskan fauna and foraminifera (from) the lower reaches of the Yenisei River; b) "dropstone," lying within diamicton and immediately underlain by a horizontal bed of pale fine grained and dark very fine-grained pulverized sand (basin of Pechora River).

Icebergs transport unsorted clastic material of various grain sizes into the polar marine basins. In the northern hemisphere their main source is Greenland, which produces 10-15 thousand icebergs each year. It has been estimated from satellite imagery that about 200 thousand icebergs exist simultaneously in the pre-Antarctic seas, with an average length of 500 m and a height above water of 50 m. The influence of ice transport of sedimentary material is such that even in deep-water depressions in the Arctic Ocean, poorly sorted argillaceous and silty argillaceous muds are formed. The hydrodynamic environment here is calm, reflecting a highly stratified water column, and bottom currents are virtually absent or occur only locally. This environment would be expected to lead to a high level of sediment differentiation and good sorting. Nonetheless the sediments are very poorly sorted, with Trask sorting coefficients (S_0) which quite often reach 5.0-5.5 [1]. In deep-water bottom sediments of pre-Antarctic regions of the Indian Ocean it reaches values of 9.2 [11]. According to Clark, pebbles, cobbles, and even boulders are transported by ice into the most remote central parts of the Arctic basin; fragments of shallow-marine molluskan species are found here. The sorting of the sea-bed sediments on the Arctic shelf is also very low: S_0 values vary mainly between 3.5 and 4.5, and reach 7 [3, 5].

Due to the influence of ice in processes of sedimentary transport, the deposits of polar seas are fine-grained, poorly sorted rocks composed of a mixture of pelitic, silty and psammitic particles with coarse clastic inclusions. These are designated by Flint (together with Sanders and Rodgers) as diamictons (Fig. 1a). In pre-Antarctic seas, where lithic fragments are carried mainly by icebergs formed from glaciers, they are distinguished by a poorly rounded, elongate form, with angular or slightly rounded margins [11].

In Arctic seas the main source of lithic material is shore ice. Since the material originated mainly from the beach it is distinguished by its limited grain-size and well-rounded form. It is not uncommon to find perfectly round specimens composed of indurated,

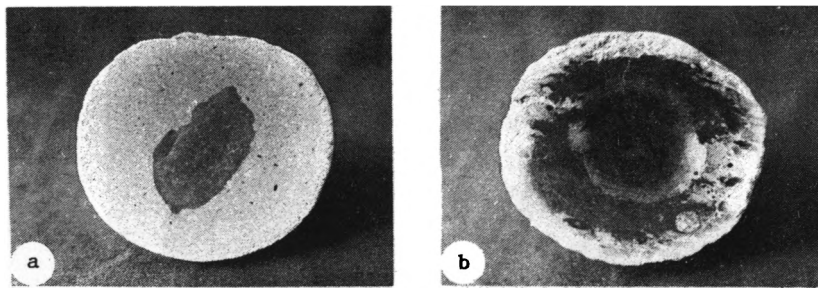


Fig. 2. Interior structure of carbonate concretions (10 cm diameter) from fine-grained glaciomarine deposits in the region of the lower Yenisei River. a) Homogeneous structure, with a dark aggregate of clay enriched in organic matter in the center; b) zoned concretion.

resistant lithologies such as quartz. In English-language literature, individual scattered lithic inclusions within fine-grained deposits have been named "lonestones," or "dropstones" where they can be shown to have fallen from above onto unconsolidated sediments (Fig. 1b). The amount of coarse lithic material within the sediments of modern polar seas varies widely. It is typically most concentrated within poorly sorted, unbedded, very fine grained diamictites, where the average proportion of psephitic inclusions is 3-5%, and sometimes reaches 30%. In better-sorted clays, bedded sands and silts, isolated cobbles, pebbles, and boulders are found. Therefore, there is a definite relationship between the lithofacies type and the proportion of coarse-grained inclusions.

The second of the main factors which distinguish the sedimentary processes in polar basins is the reduced-temperature environment. The Arctic Ocean and adjacent seas are characterized by a temperature regime which depends on the high latitude of the region with its extremely cold conditions on the one hand, and exchange of water with the neighboring oceans on the other hand. The average annual air temperature close to sea level has a negative value, reaching minimum values (-20°C and below) close to the North Pole and extending towards the Canadian Arctic archipelago. The only exception is in the western part of the Barents Sea, which is influenced strongly by the Atlantic. The southern margin of marine ice floes is defined by the isotherm of average annual air temperatures: -10 ; -15 , and more rarely -5°C . It should be noted that almost the whole of the Arctic basin lies within an area where the surface temperatures vary significantly. This emphasises the fact that the Arctic Ocean represents a "climatic landmass." The variation of average air temperature between the hottest and the coldest months is generally within the range of 20 to 30°C . By comparison, in the northern part of the Atlantic Ocean the variation in average monthly air temperature at sea level totals $6-8^{\circ}\text{C}$.

Apart from heat exchange with the atmosphere, the most significant influence on the thermal regime of the waters of the Arctic Ocean is heat exchange with neighboring oceans, together with vertical circulation, currents, and other hydrological factors. The combined operation of these factors produces temperature stratification in the water column, with three main water masses being distinguished. Close to the surface, at depths of up to $25-50$ m in the European and $75-100$ m in the American and Asian sectors, the water has negative temperature values of from minus $0-0.5^{\circ}\text{C}$ to minus $1.5-1.7^{\circ}\text{C}$. The salinity is $29.0-33.5\text{‰}$. Relatively warm, "intermediate" waters are found lower in the water column. These flow from the Atlantic and move toward the Barents and Kara seas, and to a lesser extent toward the Laptev Sea. Their salinity is $34.9-35.6\text{‰}$, and they are responsible for 42% of the heat flow into the Arctic basin. Where they enter the basin their temperature is $8-14^{\circ}\text{C}$. This reduces to 2°C in the region of Franz-Joseph Land, and in the American and Asian sectors it falls to 0.6°C . The thickness of the intermediate water mass decreases towards the east from 400 to 200 m. The Atlantic waters do not reach the eastern sector of the American and Asian sectors. Here, a relatively warm mass of Pacific Ocean water, $30-70$ m thick, underlies the negative-temperature near-surface waters. Its salinity is $32-33\text{‰}$, and its maximum temperature is 4°C .

In the Arctic basin at depths from about $800-1000$ m to the sea bed, a huge mass of water with a constant salinity of about 35‰ and negative temperatures of from -0.4 to -0.9°C occurs. Its thickness depends on the ocean-floor topography, and may reach over 3 km, more than two times thicker than the maximum recorded thickness of the negative-temperature succession on land.

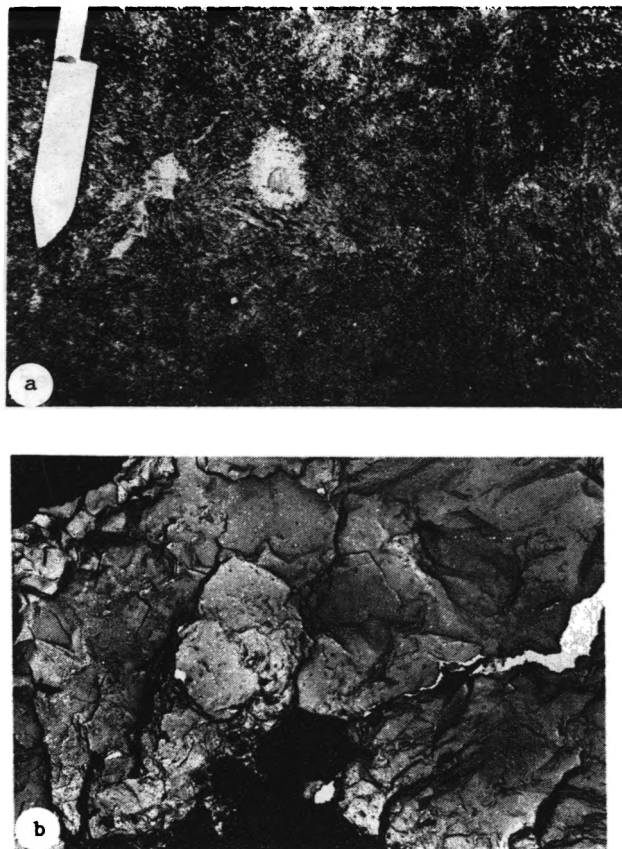


Fig. 3. Nature of iron sulfide concretions a) within a glaciomarine diamicton; and b) their interior structure at the microscopic scale. The latter is characterized by a varying degree of recrystallization of the sulfide cement: framboidal pyrite against a background of semicrystalline and amorphous material (viewed through an electron microscope). From close to the estuary of the Yenisei River, where it flows into the Kara Sea.

The bottom sediments in the deep-water part of the ocean therefore also have negative temperatures, but they are saline and therefore in a liquid or viscoplastic state. At depths of several or a few tens of centimeters from the sediment surface they are already desiccated and compact. The thickness of sediments with negative temperatures in the ocean bed has not yet been established.

In the zone of polar shelf seas, near-surface waters down to depths of 15-20 m experience substantial seasonal temperature fluctuations, becoming positive (averaging 3-5°C) in summer, and negative in winter. Below these is a water mass with constantly negative temperatures, reaching -1.5 to -1.8°C in Arctic seas [7]. In pre-Antarctic seas this water mass is typically characterized by a temperature between -0.5 and -1.5°C and a high salinity (~34.5‰). It forms during the intense cold of winter in the zone of stationary polynia within shore ice. These are characterized by extremely low water temperatures (to -1.9°C) and high salinities (34.7‰).

The negative temperatures of the bottom waters in polar seas present the possibility of successions affected by permafrost being preserved below them for extended periods as the land surface is flooded during a transgression. There are a number of cases recorded [1-3, 5, 9 et al.,] of cryogenesis affecting the diagenesis of permanently frozen rocks, and the geochemical and mineralogical processes operating within them.

Distinctive features of sediment formation in cold polar seas have been noted by Klenova, Gorshkova, Saksom, et al. The main effect of the low temperature environment is that the sediments are predominantly terrigenous. Biogenic and chemogenic sediments almost never occur [1, 2, 9 et al.,]. The carbonate content, usually biogenic calcite, does not usually exceed 5% in the Barents Sea, 5-10% in the Kara Sea, and 1-2% over most of the Laptev Sea.

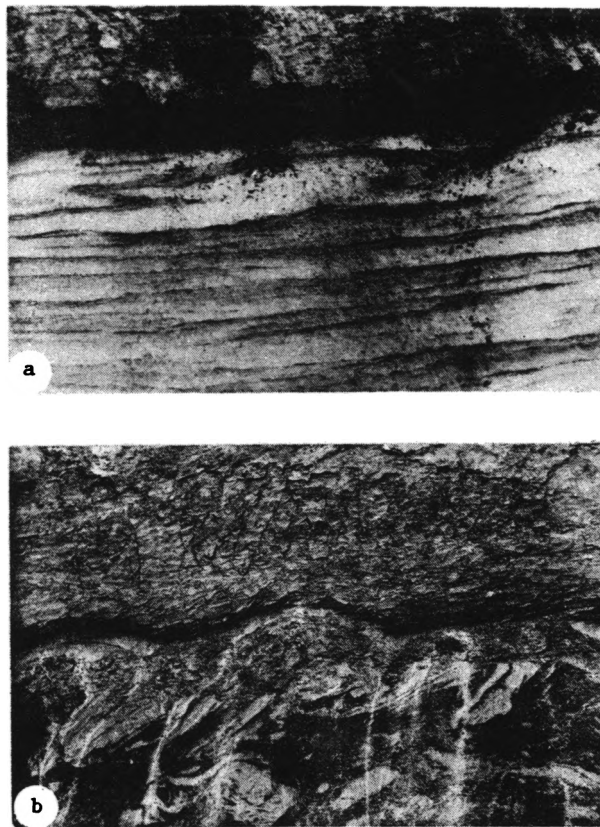


Fig. 4. Conformable contacts between underground ice of bedded-lensoid type and the surrounding fine-grained glaciomarine deposits (from the Gydansk Peninsula in the north of western Siberia). a) Horizontally bedded ice overlain with a horizontal contact by lumpy fragmented clays (field of view 2×3 m); b) plicate folds in ice, overlain by a wavy contact at the base of clays which are penetrated by a network of fine ice-filled schlieren (field of view 4×6 m).

In the northern deep-water part of the Laptev Sea, influenced by warm Atlantic waters, the carbonate content reaches 4%. The value in the East Siberian and Chukchi seas is 0.5-2.0%, although in the regions of the Chukchi Sea influenced by relatively warm positive-temperature water from the Bering Sea it increases to 3%. In the Bering Sea itself, according to Lisitsyn, proportions of biogenic CaCO_3 reach 18.1% in silty-argillaceous muds, 35.2% in coarse siltstones, and 40.43% in fine sands. Areas of the central Arctic Ocean with increased concentrations of biogenic carbonate (up to 30% and more) coincide with the continental slope and submarine ridges affected by the intermediate positive-temperature water masses originating from the Atlantic. In deep-water troughs, the proportion of CaCO_3 varies from 1 to 5%.

Virtually none of the sediments in the Arctic seas and ocean contain accumulations of siliceous organisms, and chert is usually absent. The proportion of authigenic silica within the sediments is usually a fraction of a percent. However, in the eastern part of the Chukchi Sea, influenced by the Bering Sea waters, the content of authigenic silica increases up to 10% due to the presence of the remains of diatomaceous algae. By comparison, the content of authigenic silica in bottom sediments of the Bering Sea (according to Lisitsyn) reaches 37% in argillaceous muds, with an average of 25%.

A reduced content of the main rock-forming biogenic components, both siliceous and carbonate, which play an important role in other climatic zones of the world ocean, is a characteristic feature of the sediments of polar basins. Despite the generally low proportion of dispersed authigenic carbonates within the modern bottom sediments of Arctic seas, Saksom has noted neoformed calcite occurring as fringes of fine crystals on the surface of other minerals and rock fragments, and also occasional pellets and spherulites. The diagenetic redistribution of fine-grained carbonate within buried sediments takes place, and concentrates

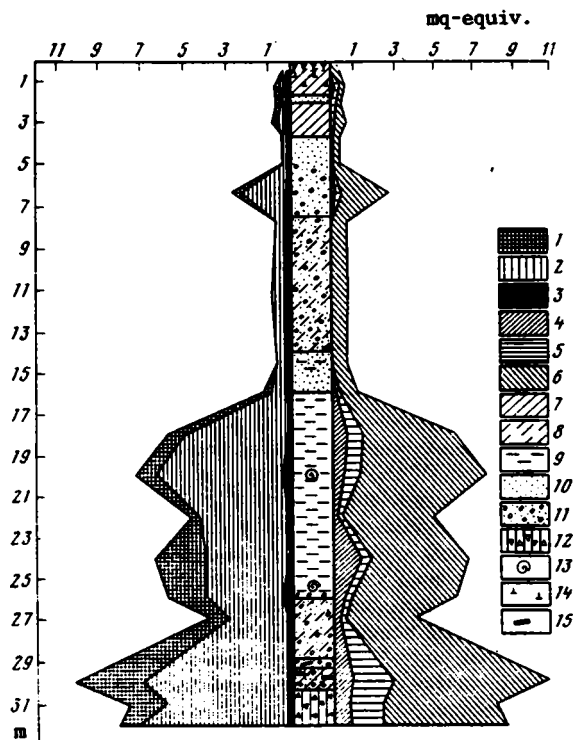


Fig. 5. Graph of the distribution of water-soluble salts through a section of frozen shelf sediments underlain by bedrock (Chukchi Sea coast). 1) SO_4^{2-} ; 2) Cl^- ; 3) HCO_3^- ; 4) Ca^{2+} ; 5) Mg^{2+} ; 6) $\text{Na}^+ + \text{K}^+$; 7) loam; 8) sandy loam; 9) silt; 10) sand; 11) pebbles, cobbles; 12) eluvial bedrock; 13) marine mollusk shells; 14) peat inclusions and interbeds; 15) lignitized plant remains.

locally to form concretions [3, 5]. These are characteristic of Pleistocene glaciomarine sands, loams, and clays. The concretions are dense, usually rounded, spherical, oval, ellipsoidal, and occasionally tubular. They are usually less than 10-15 cm in size, but sometimes reach up to 50 cm in diameter. They are generally found scattered throughout the rock, although sometimes they form groups of 5-7 specimens. The interior structure of the concretions (Fig. 2) is either homogeneous or zoned; the microtexture is homogeneous, reticulate, lattice-like, or flakey. They are composed of the same sandy-argillaceous terrigenous material as the surrounding rocks, with inclusions of pebbles and cobbles, but cemented by carbonates which form 50-70% of the concretion. The carbonate cement is of a porous or basal type, and comprises calcite, manganese-bearing calcite, manganocalcite, occasionally calcified dolomite, and in several cases, siderite [8]. The main components of the carbonate cement reach the following proportions: CaCO_3 , 58.6%; MnCO_3 , 14.52%; FeCO_3 , 29.03%; MgCO_3 , 9.71%. Different mineral compositions have been noted in the central and outer zones of the concretions.

It has long been recognized that sediments of polar seas from depths of just a few centimeters from, and sometimes virtually at, the sediment surface have a grey color and are characterized by a chemically reducing environment. This is due to the presence of dispersed decomposing organic matter. The C_{org} content varies mainly from 0.5-1%, and occasionally reaches 1.5-2.0%. In shallow-water embayments (such as the Laptev Sea) it can reach 3%. These proportions of dispersed organic matter are quite sufficient for reducing conditions to arise in the sediment during diagenesis [14]. This results in the reduction of iron oxides, manganese oxides, and sulfates, and the generation of sulfides. The formation of diagenetic minerals within Pleistocene glaciomarine clays, loams, and occasionally in silts and sands produces concretions of iron oxide (Fig. 3a), which are nucleated around organic remains. The margins of some of the concretions are distinct, whereas other concretions are formed only incipiently and pass gradationally into the surrounding rock. The concretions have rounded outlines, being either oval, spherical, ellipsoidal, or irregular, and are 5-7 cm in diameter. The most well-developed concretions have a zonal structure, with a pyritic core surrounded by black amorphous material (hydrotroilite). The iron sulfides cement clastic



Fig. 6. Cryogenic network texture with a high ice content within glaciomarine clays which underlay water-bearing sediments before freezing of the sediments.

grains of sand and silt, together with argillaceous material. The cement is of basal type, or occasionally porous. The concretions are centered on dead marine organisms or plant remains. The sulfides replace and corrode grains of clastic material; pyrite typically develops along the cleavage of hydrobiotite. The sulfide cement has in turn suffered fracturing which has been infilled by carbonates to form either a network or individual small veinlets [9]. The proportion of iron sulfides within the concretions reaches 24.63%, with 28.55% sulfide, and C_{org} reaches 4.02%.

Study of the concretions under the SEM allows the stages in the formation of the crystalline structure from an initial colloidal gel of iron sulfide to be established. Shaposhnikova has recognized a transitional series of structures from colloform to crystalline grains, passing through various stages of framboidal iron sulfides which finally form perfectly crystalline framboids (Fig. 3b). The data show convincingly that an initial phase of colloidal iron sulfide plays a part in the development of the concretions. The isotopic composition of sulfur within the pyrite [5] shows that light isotopes dominate, indicating that the pyrite formed by microbiological sulfate reduction of pore waters in the marine sediments to form sulfides. Spherical concretions of vivianite, 1-5 mm in size, are also a typical diagenetic product of shelf deposits in polar seas, and these also form pseudomorphs of organic remains.

The modern sea-bed sediments of Arctic seas are still in the initial stages of study, but they contain iron oxides and iron-manganese concretions with Fe_2O_3 contents of up to 25% and MnO up to 12%. Bacteria play a vital role in their formation. Concretions form in the initial (oxidizing, according to Strakhov) diagenetic stage in the sediments, and are usually dissolved in the subsequent reducing stage. The oxides of iron and manganese are transformed into mobile ferrous forms and diffuse into the overlying marine waters. Therefore, fine-grained Pleistocene glaciomarine deposits which are relatively rich in dispersed organic matter pass through a stage of reduction during diagenesis, and concretions of oxides are not preserved. Such concretions are only typical of coastal sands and sandy-gravel facies where diagenesis takes place in well-aerated conditions. These concretions are spherical or occasionally globular. Iron and manganese hydroxides often cement whole lenses and lens-like interbeds, and fractures in sands and gravels.

The data on dispersed authigenic minerals and concretions show that, despite the low, dominantly negative, temperature conditions the diagenesis of sediments in polar seas includes authigenic mineralization and redistribution of newly formed material with its subsequent reprecipitation and concentration. The geochemistry of the diagenetic process leads to concentrations of newly formed mineral components usually not exceeding 50% of concretions, or occasionally 70%. The remainder is composed of clastic particles. Within fine-grained terrigenous sediments in temperate and hot climatic zones, authigenic iron sulfides and carbonates often form 100% of concretions. Siliceous concretions are also common in these sediments, but they are completely absent from cold-water deposits of polar seas.

The dominant clay minerals in the deposits of polar seas are hydromicas (illites, and occasionally hydromuscovites and hydrobiotites), and montmorillonite. These may be mixed with kaolinite, beidellite, hollow tubes of halloysite, chlorite, fine spicules of magnesium

silicates, and fine-grained quartz [3]. One of the geochemical characteristics of diagenesis in cold-water polar seas is that carbon dioxide given off during the decomposition of organic matter is not neutralized within the sediment pore fluids with the precipitation of carbonate (as occurs in warm seas). The pore fluids in polar basins are aggressive, with a high carbonic acid content, and they dissolve the silicate minerals. This is a characteristic of clay mineral authigenesis in the polar basins. On the shelf, hydromicas are transformed into montmorillonites and beidellites. In deep-water zones of the Arctic Ocean, neoformed mixed-layer clay minerals of hydromica-montmorillonite composition have been recorded. Lower in the sedimentary section the proportion of diagenetic magnesium silicates increases, and hydromicas are transformed into beidellite [1]. The stages in this process can be observed under the SEM: Isometric, sharply angular plates of hydromica acquire indistinct outlines, forming flakes with swollen margins.

The negative temperatures of the bottom sediments in polar seas lead to the most striking and characteristic features of their diagenesis — the role of cryogenic processes. The most recent studies of the Arctic shelf, using geophysical methods and deep drilling, have shown that the bottom sediments have a complex cryogenic structure, and that their physico-mechanical state lies at an extremely unstable position at the phase transition between water and ice. The role of cryogenesis within the general diagenetic history, and the conditions on the polar shelves, is only just beginning to become clear and to be interpreted. However it is already clear that its role is of no little significance.

According to experimental data [12], the process of freezing in fine silty muds (with 25% of the <0.01 mm fraction) with a 2% salinity begins between -1.2 and -1.3°C ; with a 4% salinity it begins between -2.4 and -2.6°C ; and with a 5% salinity, at -3.2°C . The muds pass into a frozen state at between -1.6 and -1.7°C with a salinity of 2%; and between -4 and -5°C with a salinity of 4-5%. Since the temperature of marine waters in polar seas does not fall below -1.9°C , and the salinity of bottom-sediment pore fluids is usually higher than that of the overlying marine waters, the pore fluids will be at a negative temperature but not frozen solid. They are either liquid, semiliquid, or viscoplastic. Bottom sediment successions with highly mineralizing negative-temperature pore fluids (salinities of 50-100 g/kg or more) are widespread.

It is currently widely thought that the accumulation of sediments and the physicochemical and diagenetic transformations which take place within them in polar seas occur with pore waters in the fluid state. They do not freeze until after the sediments are drained and exposed at the surface. However, a number of factors and observations of the cryogenic structure of successions of glaciomarine deposits show that the underground ice contained within them formed partially in the sea-bed environment during cryogenic-diagenetic transformations. The distribution of underground ice with a lensoid or bedded form is particularly indicative of this. The thickness of these beds reaches 50 m, sometimes extending to hundreds of meters, and may even reach several kilometers. They occur at various depths from the surface (100-150 m or more). Some of the beds show all the signs of a sedimentary rock: horizontal and horizontal-wavy bedding, caused by interbedding of clean layers of ice with layers rich in terrigenous particles; inclusions of lithic fragments and remains of marine fauna, conformable contacts with the surrounding rocks (Fig. 4); and also erosive contacts with the basal beds of overlying or onlapping successions, etc. In order to explain these structures and the conditions in which they arose, the hypothesis has been advanced that they formed as a result of successive stages of freezing of the sea floor, with varying amounts of terrigenous material being frozen within the ice [3, 5]. This process may take place, for example, where the sea-bottom waters have a reduced salinity, and at the same time undergo a significant drop in temperature to a temperature below the critical point where fluids of their salinity freeze.

Ice deposits which display plicate folds are widely distributed in successions of shelf deposits from polar seas. In some cases the folding is secondary, and is related to the plastic properties of the ice under the influence of changing loading and pressure. In many instances, however, the disposition of the deposit indicates that the process of folding occurred during the formation of the surrounding deposits, and was therefore synsedimentary [4]. The bodies of ice, together with the folded beds of rock immediately above, are overlain by unfolded deposits with a normal dip. In other words, the folding disappears upwards in the section, the degree of folding within the succession decreasing until it is completely unfolded. This shows unambiguously that the folding occurred during sedimentation. Two hypotheses have been put forward to explain the relationship between the ice formation and the folding of sediments in the sea bed environment.

One of these hypotheses [13] suggests that lenses and beds of ice of the type described originate from mudslides and landslips of negative-temperature water-saturated marine sediments. Spontaneous breakdown of the stable state causes the coagulative bonds to weaken, leading to the complete destruction of structure in the fragile framework. Subsequent hydrophilic coagulation of the suspension, which contains a large amount of weakly-bound water, leads to the liberation of the water. The liberated water is separated from the mineral framework, and most of it accumulates at the margins of the lithologically heterogeneous beds. The freezing temperature of the liberated water is higher than the sea-bed sediments, so being within a negative-temperature zone it freezes into ice and forms lensoid and bedded layers within the folded sedimentary successions.

One of the serious weaknesses of this hypothesis is the fact that it does not explain the commonly observed extremely fresh-water composition of the ice, or its meteoric rather than marine isotopic composition.

According to the other hypothesis [6], the formation of layers of folded underground ice of bedded-lensoid form is related to artesian water being introduced in stages into the succession of unconsolidated bottom sediments on polar shelves, and to its freezing in the negative-temperature zone. This also explains the fact that the deposits are folded during the formation of the surrounding sediments, the usually ultrapure chemical composition of the ice, and its atmospheric-continental origin.

It is considered that the transition to the frozen state in the sea-bed environment occurs in local areas due to a special combination of favorable factors. The main successions of marine shelf sediments become frozen after rising above sea level, from the top downwards (starting from the surface). Until this happens, the pore fluids within them undergo diagenetic transformations to varying degrees. On freezing they can be subdivided into a solid phase within the newly formed frozen successions, and the frozen-out brines. Into the solid phase, depending on the temperature of the succession and its salinity, pass carbonates (calcite) and sulfates (mirabilite, gypsum); i.e. the frozen marine sediments undergo carbonatization and sulfatization. As the shelf sediments are frozen from above, a process of cryogenic concentration of the water-soluble salts occurs with movement down through the section, with the result that the lower parts of the frozen marine succession are enriched in salts (Fig. 5). If the base of the frozen rocks overlies poorly or intensely fractured bedrock, they will be penetrated by the highly mineralizing capacity of 140-160 g/liter saturate friable rocks immediately underlying fine-grained frozen marine sediments [2]. The sediments are impoverished in the most soluble salts, especially where they have been repeatedly frozen and thawed. Fine-grained shelf sediments become saturated with fresh water when their freezing is accompanied by abundant ice-segregation schlieren (Fig. 6), and they are most abundant where there is a source of underground fresh water. Layers of ice in this situation are virtually fresh, and the salinity even of marine sediments is very low [5]. The most extensive freshening of pore fluids (with salt contents down to a few tens of milligrams per liter of water) is attained in bedded ice deposits formed from fresh underground waters in water-bearing horizons. Therefore, the freezing of successions of shelf sediments leads to the redistribution of water-soluble salts within them, with a variation not only in their proportions but also in their nature.

As a result of the complex combination of cryogenic and diagenetic geochemical transformations within the shelf sediments, the final mineral composition varies. A comparison of data on the chemical composition of pore fluids from modern bottom sediments in Arctic seas with the composition of the most soluble salts within Pleistocene glaciomarine deposits shows that they are sometimes similar and sometimes significantly different. However, they have similar characteristics, suggesting that indications of the primary marine salinity are preserved within the frozen marine sediments [3, 5].

One particular product of the submarine cryolithic zone are gas hydrates. A combination of factors allows them to form in the sea floor environment. The most important of these is that the combination of temperature and pressure values needs to be at defined levels. Furthermore, the proportion and origin of the gas itself has an influence on the process of gas-hydrate formation. Important factors include the gas composition; the composition and salinity of the associated water; the lithological composition, structure and texture of the surrounding sediments; the amount and type of dispersed organic matter within the sediments; and the nature of the interactions between the gas molecules and the water. The history of the cryozone in the various parts of the shelf, and increases and decreases in the temperature of the frozen succession, also play an important role in the formation of gas hydrates.

Therefore, the data described here show that the characteristics of sedimentary rock formations within the sedimentary basins in polar areas are caused by the low temperature environment and the influence of the ice factor. The latter leads to distinctive forms of cryogenic lithogenesis. This influence results in the accumulation of highly distinctive, poorly sorted, primarily fine-grained terrigenous sediments with coarse clastic inclusions of a diamicton type, and also homogeneous argillaceous-silty muds in areas covered with stable floating ice, even in shallow water. The reduced-temperature conditions have an effect on all stages of development of sedimentary rocks in polar seas: during sediment accumulation and diagenetic and epigenetic transformations. The temperature factor is responsible above all for the terrigenous composition of the sediments, and for the possibility of frozen rock successions being preserved below the sea bed for geologically significant periods after they have been submerged by the sea, and for the formation of perennially frozen rock formations in certain conditions in shallow water. The low temperature results in aggressive pore fluids being present during sediment accumulation, and the possible occurrence of clay mineral growth, and also the formation of distinctive authigenic minerals and concretions. These are distinguished by the absence of neoformed chert, and the low proportion of authigenic carbonates, sulfides and iron phosphates. The incomplete process of redistribution of dispersed authigenic minerals is indicated in the composition of diagenetic concretions, which contain a large proportion of terrigenous material, commonly predominating over the concretionary cement. The negative temperature environment during the stages of sediment genesis and diagenesis, and the extremely unstable physical condition of the bottom sediments, which lie on the water-ice phase transition, lead to the possibility of buried ice and bodies of frozen ground developing during the formation of the sediments. Finally, epigenetic (superimposed, post-diagenetic) freezing of successions within sedimentary basins leads to the final cryogenetic transformations.

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SEDIMENTARY ASSOCIATIONS IN THE RIPHEAN SECTION, SOUTHERN URALS

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A number of major terrigenous and carbonate complexes have been recognized in the Riphean stratotype on the basis of detailed lithologic and facies analyses on the Bashkirian meganticlinorium. These sedimentary complexes appear to be combinations of proximal facies and macrofacies that are locally related to both environments of deposition and certain stages in the evolution of the sedimentary basins. The main features of the evolution of the Riphean sedimentary basins on the west slope of the Southern Urals can be reconstructed from a study of the vertical sequence of these complexes. It is proposed that the tectonic setting of the early and middle Riphean in this area differs from that of the upper Riphean. The make-up of the Karatau series is shown to be very similar to the Siberian platform and pericratonic Riphean.

The current literature contains numerous stratigraphic models for the subdivision of the upper Precambrian deposits on the west slopes of the Southern Urals [2, 5, 8, 19, 20, 27, 45, 52 etc.]. On the basis of these models of the late Precambrian development of the Bashkirian meganticlinorium, it is impossible to decipher the evolution of the many-kilometer-thick Riphean-Vendian sedimentary megacomplex. Most of these models, among which three major groups can be identified, are to some degree simplistic.

In the first group of models the crustal evolution of this region and the associated sedimentation are considered to be a single, directed geosynclinal cycle that includes the entire array of deposits, from the lower Riphean Aisk suite to the Vendian Ashin series [5, 6, 52, 55]. Publications in the second group attempt to show that crustal evolution and basinal sedimentation on the west slope of the southern Urals during the late Precambrian involved several sequential geosynclinal cycles [2, 12, 50, etc.]. In recent years the concept of a polycyclical rift-depression evolution of the Urals during Riphean has appeared in much of the literature [17, 18, 27, 43, 46, etc.].

So far, however, virtually none of these studies have been based on detailed facies analysis of the Riphean stratotype, the thickness of which is about 70-80% of the total thickness of the entire section. Sometimes this leads to a completely artificial construction of formational units [2, 27, 45, etc.] and of their grouping in the section, and thus to an essentially incorrect interpretation of both the environments of deposition and the late Precambrian evolution of the region.

The present article attempts to approach the problem of analysis of the deposition and history of the Riphean stratotype sequence by a different route: a consideration of the basic features of the various depositional basins through time on the basis of detailed lithologic and facies study of the sedimentary rocks [3, 23, 28-37, etc.]. This is all the more interesting in that it provides a single methodological basis for future comparative analysis of the tectonic style of various Riphean sedimentary basins in the southern Urals and Siberia, and the determination of their general and specific evolutionary features.

The presently available data on the environments of deposition and composition of the upper Precambrian deposits on the west slopes of the southern Urals [33, 37, etc.] indicates that the origin of the sediments in the Riphean section changes markedly from the base upward. The depositional environments of the carbonaceous deposits [31], nonquartzose and volcanic sediments, and variegated terrigenous and carbonate rocks, taking into account that the Riphean series in the southern Urals are unconformable and that the basal beds are con-

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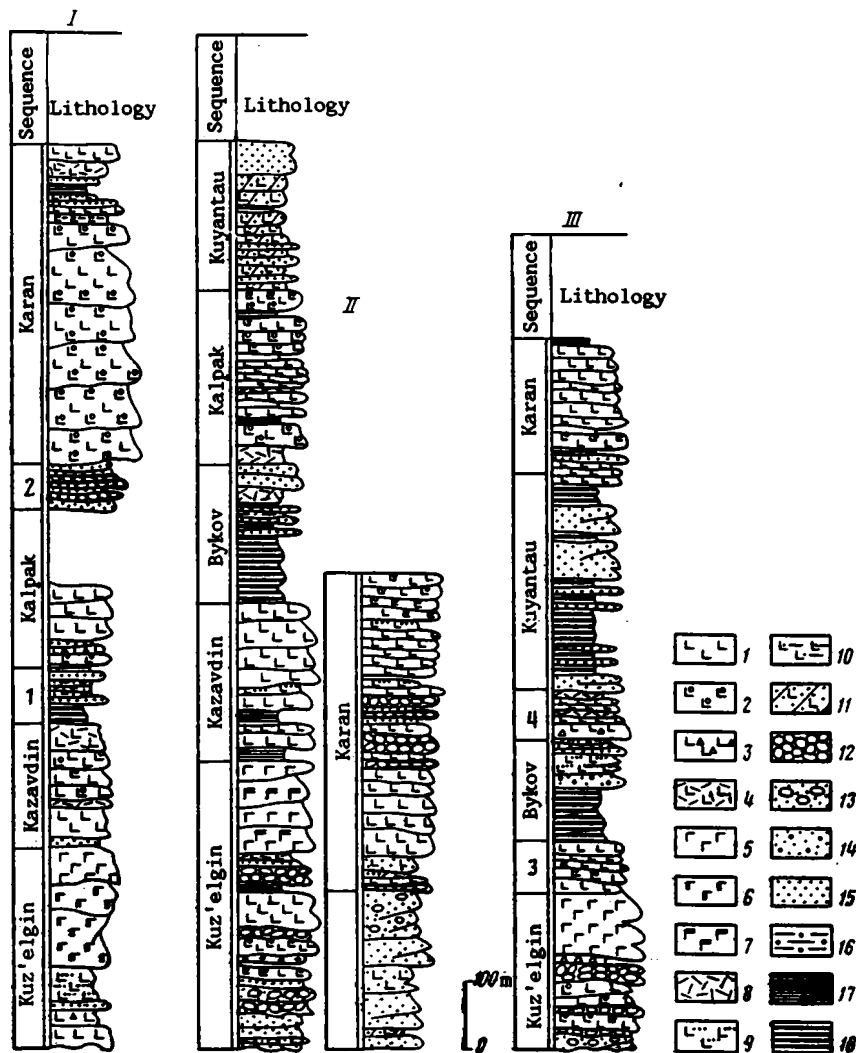


Fig. 1. Columnar sections of the volcanic-terrigenous complex, mainly continental and nearshore deposits (Mashak level of the middle Riphean Yurmatin series) [43]. 1) Metabasalts; 2) amygdaloidal metabasalts; 3, 4) basic lava breccias and tuffs, respectively; 5) rhyolites; 6) trachyrhyolites; 7) quartz porphyry; 8) acidic tuffs; 9) tuffaceous sandstones; 10) tuffaceous siltstones; 11) tuffaceous argillites; 12) conglomerates; 13) sparse-pebble conglomerates and grits; 14) coarse-grained sandstones; 15) fine- and medium-grained sandstones; 16) siltstones; 17) argillites; 18) same, with high content of organic matter. Sections: I) Mashak Ridge; II) Bol'shoi Shatak Ridge; III) Kukhtur River basin.

tinental in origin, suggest that deposition of different types took place in the lower, middle, and upper Riphean.

The Riphean stratotype on the west slopes of the southern Urals includes volcanic, terrigenous, and carbonate deposits of the Burzyan, Yurmatin, and Karatau series [7, 47, 51, etc.]. Their general nature, composition, and stratigraphic details have often been described in the literature (see references in [33, 37, 51, etc.]). The textural features of the terrigenous and carbonate rocks have also been well described [1, 4, 9, 10, 13, 23, 37, 41, 43, 48, 53, etc.], and together with geochemical data [11, 26, 33, 35, etc.], readily reveal the origin of the various formations.

Detailed facies analysis of the Riphean deposits of the Bashkirian meganticlinorium shows that they include a whole gamut of sediments deposited in a wide range of conditions. On the basis of a study of the texture of the rock, the type of sediment, and the facies, and taking into account data on the paleoclimate and paleotectonic conditions in the Riphean stratotype, a number of major terrigenous and carbonate complexes of various origins can be recognized. These are understood to be an assembly of similar facies and macrofacies that

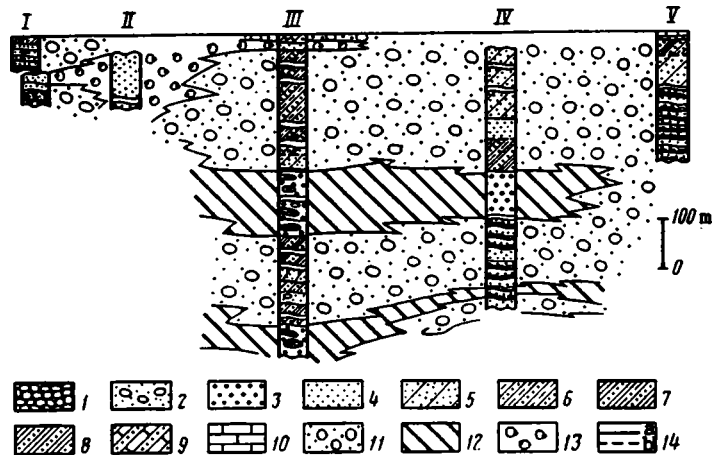


Fig. 2. North-south section through the terrigenous, mainly continental (alluvial to deltaic) assemblage (Biryan level of the upper Riphean Karatau series). Facies based on [33]. Lithotypes: 1) conglomerates, 2) sparse-pebble conglomerates, 3) medium- and coarse-grained sandstones, 4) fine-grained sandstones, 5) coarse-grained siltstones, 6) interbedded siltstones and sandstones, 7) interbedded clay shales, siltstones, and fine-grained sandstones, 8) alternating clay shales and fine-grained sandstones, 9) alternating terrigenous and carbonate rocks, 10) limestones. Associations of Various Origins: 11) terrigenous, mainly continental, alluvial to deltaic, 12) terrigenous, very shallow water origin, 13) shallow marine terrigenous, 14) Contacts: a) sharp; b) gradational. Sections: I) Kyzha River, II) Bol'shoi Nugush River, III) Mal'yi Inzer River to the town of Kumbino, IV) Yuryuzan' River below Ekaterinovka, V) Satka River at Poroga.

are related in place and depositional environment and that correspond to a certain stage in the evolution of the sedimentary basin. A brief description of these assemblages is presented below, and the main aspects of their distribution through the section are examined. Reconstruction of the lateral relationships is done for the upper Riphean only [33]. A similar model for the entire Riphean is a problem for the near future.

Terrigenous deposits form five major lithofacies assemblages.

The volcanic-terrigenous assemblage, primarily continental and nearshore deposits, is characteristic of the Navysh-Chudin level of the lower Riphean Aisk suite and the six lowest subsuites of the middle Riphean Mashak suite. It consists of intermixed conglomerates, grits, and sandstones with various types of inclined bedding, mostly unidirectional; interbedded sets of shale, sandstone, and siltstone with desiccation cracks and ripple marks; and small scours. These rocks are accompanied in the section by basic and acidic volcanics that tend to be alkaline (Fig. 1). This assemblage formed on alluvial-deltaic and nearshore-continental plains, a piedmont fan system (according to V. I. Popova), and open coastal waters. Lithologic study shows the presence of channel deposits, river mouth sediments, floodplains, intermittently exposed lagoons, nearshore conglomerates, proluvial-deluvial deposits, etc. [37, 43, etc.]. Rapid transition from conglomerates to fine-grained terrigenous sediments or basalt flow is characteristic of the section.

Acid and basic volcanic rocks are associated mainly with continental facies in this assemblage [41, 43, etc.]. The amount of these rocks varies markedly from section to section; i.e., they constitute from 30 to 60% of the total thickness of the Mashak suite in the central part of the Bashkirian meganticlinorium [41, 43].

The formation of this assemblage was characterized by a rather varied paleogeographic setting in the depositional basin, the predominance of continental and nearshore deposits, and probably a high relief in the erosional zone. These deposits tend to represent the earlier stages in the development of the early and middle Riphean basins, and as recent studies have shown, were probably formed during a rifting event. The distribution of REE in volcanics of both the Aisk and Mashak suites indicate a platformal environment [43].

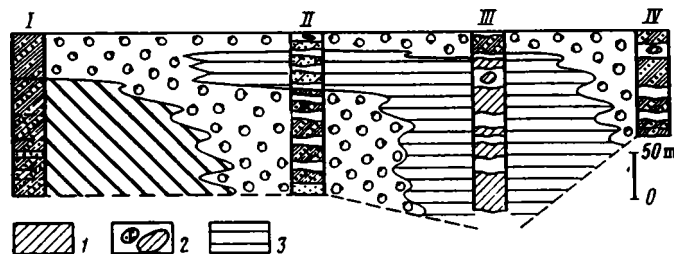


Fig. 3. North-south section at the Nugush level of upper Riphean deposits, Bashkirian meganticlinorium, showing the relationship between very shallow terrigenous, shallow marine, and marine (offshore) sedimentary associations. 1) Fine-grained siltstones, 2) rock type in covered intervals, 3) offshore terrigenous marine sediments. See Fig. 2 for other lithologic symbols. Sections: I) Kuzha River, II) Malyi Inzer River at Kumbino, III) Yuryuzan' River above Ekaterinovka, IV) Satka River at Poroga.

Depositional environments of the rocks in this assemblage during the early and middle Riphean were probably rather varied, however. This is suggested by differences not only in thickness, but also in the overall conditions: In the early Riphean grabens formed in the rigid Archaean to early Proterozoic basement, while at the beginning of the middle Riphean, they formed in the Burzyaniya sedimentary complex. It should also be noted that, unlike Cenozoic rift zones, where two sequential associations can be reliably recognized, the fine-grained and coarse-grained (actually taphrogenic) associations, no such a sequence has been found in the Riphean section. In our view, despite the comprehensive geochemical and petrologic data, this makes a direct analogy impossible between Cenozoic epiplatformal rift zones and the structures formed in the area of the present Bashkirian meganticlinorium at the beginning of the early and middle Riphean [43].

The terrigenous, mainly alluvial to deltaic assemblage is restricted to the base of the upper Riphean Karatau series. It consists of medium- to coarse-grained arkoses, graywackes, and feldspathic-quartzose sandstones and siltstones with conglomeratic interbeds (Fig. 2). This assemblage was formed during a relatively quiet tectonic period in an area of compensating differential downwarp of the basin [1, 29, 33]. It contains a varied group of facies: channel fill, floodplain, interfluvial, ephemeral lake, shifting shallows at river mouths, etc. The extensive distribution, varied facies, and textural features of the rocks [33] indicate that we are dealing with a large complex in the area of the mouth of a branching (multichannel) river system. The occurrence of this complex at the base of the upper Riphean clearly indicates the appearance of a regressive phase at the middle-upper boundary, with a significant (if not complete) contraction of the marine basin. This suggests that there was a sharp change in the style of sedimentation at the beginning of the late Riphean. The sediments of this assemblage indicate the introduction of only a small amount of clastic material, which was being eroded from a broad drainage basin of moderate to low relief composed of sedimentary, metamorphic, acidic magmatic, and to a minor degree, basic magmatic rocks [1, 9, 40, and others]. Lithologic and geochemical data show the prevalence of a semiarid climate [11, 35].

The very shallow water terrigenous assemblage also includes a rather broad spectrum of sediments, formed during periodic to frequent exposure [34]. It includes sandy, silty, and clayey sediments of an open marine to semirestricted, highly dissected shoreline and periodically exposed bays and lagoons; and nearshore to continental deposits associated with alluvial and deltaic environments, as well as sediments of the sublittoral mobile zone of the shallow marine shoreline. Typical structures include numerous and varied types of ripple marks and desiccation cracks, wavy bedding of migrating ripples, scour-and-fill, pseudomorphs after halite, variously oriented small- to medium-scale crossbedding, reactivation surfaces, lenticular crossbeds and flaser bedding, etc.

In most of the sections in which this assemblage was examined, no shoreline indicators or clear-cut continental deposits were found, which indicates that the sediments were formed in a flat, extremely shallow basin with shoals and banks, and areas of periodic exposure that varied in location and extent, etc. (Fig. 3). Low-amplitude fluctuations in water level in this environment caused considerable changes in the extent of the various zones.

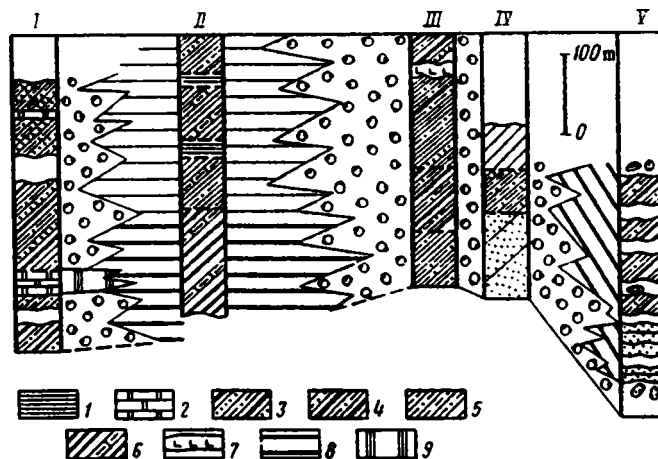


Fig. 4. North-south section of the Maloinzer level of the Middle Riphean Aisk suite, which illustrates the interrelationship of very shallow and shallow marine deposits (somewhat enriched in organic matter) with fine-grained terrigenous deposits formed far offshore. Lithotypes: 1) argillites, shales; 2) dolomites; 3) alternating carbonaceous shale, siltstones, and fine-grained sandstones; 4) interbedded siltstones and carbonaceous shale; 5) alternating fine- and coarse-grained siltstones; 6) carbonaceous shale with sparse thin interbeds of clayey limestone; 7) gabbro or diabase dikes. Associations of Various Origins: 8) fine-grained terrigenous marine sediments with organic matter; 9) marine carbonates. See Fig. 2 and 3 for other lithologic symbols. Sections: I) Kuzha River, II) Zigazino-Komarovsk region, III) Katava River above Katava-Ivanovsk, IV) Yuryuzan' River at the mouth of the Bulanka River, V) Malyi Bagrush Creek.

Very shallow-water terrigenous deposits are known from virtually every level in the Riphean deposits of this area [34]. They are most abundant in the middle Riphean.

The shallow marine terrigenous assemblage includes sandstones in a range of grain sizes and bedding styles. There are units of alternating sandstones, siltstones, and shales with various types of undulating bedding and with no signs of periodic exposure. Based on the composition of the sediments and their position in the section, a number of varieties can be recognized.

The first of these is a sequence of irregularly alternating sandstones, siltstones, and shales or glauconitic quartzose and feldspathic sandstones and siltstones. These deposits were formed under relatively stable conditions tectonically, in hydrodynamically varied shallow marine zones [30]. Abundant glauconite is known to result from optimum climatic conditions, proximity to land, and widespread transgression [38 etc.]. We may thus conclude that the widespread occurrence of these deposits at the Inzer level of the upper Riphean is characteristic of the appearance of a broad marine shelf.

The second type of shallow marine deposits is similar to the gently undulating, alternating sandstones, siltstones, and shales described above, but with no glauconite. They occur in a number of lower and middle Riphean sections (Fig. 4) and probably formed in basins smaller than those in the late Riphean, so that conditions were generally unfavorable for glauconite.

The third type of sediment consists of sequences of alternating siltstones and carbonaceous shales with minor interbeds of sandstone (see Fig. 4). Deposits of this type can be found in the Avzyan, Zigazino-Komarovsk, Yushinsk, and Bol'sheiner suites and in a number of other levels of the lower and middle Riphean [31]. The sandstones and siltstones are similar in structural features to the sandstones and siltstones described above (thin horizontal crossbedding and wavy bedding, ripple marks, lack of desiccation cracks, etc.); the hydrodynamic environment was thus very similar, and probably only the climatic conditions were different.

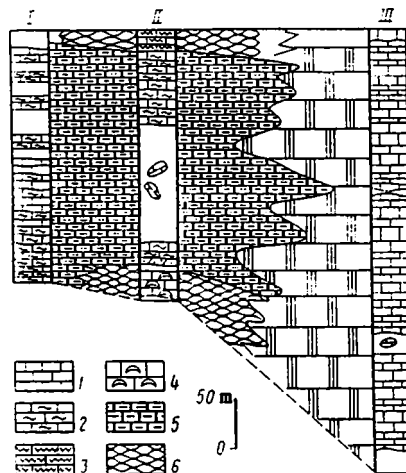


Fig. 5. East-west section of the Katava level, upper Riphean of the Bashkirian meganticlinorium, showing the relationship of phytogenic and chemogenic shallow marine and marine carbonate rocks. Lithotypes: 1) limestones, 2) clayey limestones and marls, 3) striated algal limestones, 4) stromatolitic limestones. Associations of Various Origins: 5) shallow marine carbonates, mostly variegated, 6) shallow marine carbonates, mostly phytogenic. See Fig. 2-4 for remaining lithologic symbols. Sections: I) Zilim River at Tolparovo, II) Bolshoi Inzer River (from V. A. Filippov), III) Tirlyan River (from A. Z. Syundyukov).

The fourth and last type of shallow terrigenous marine sediment includes rather thick and monotonous units of sandstones and (or) siltstones, which are found in the Lemezín subsuite of the Zil'merdak suite and in the Zigal'gin, Yushin, and Mashak suites. In the latter two levels it is primarily gray and greenish-gray sandstones with thin interbeds of siltstone and carbonaceous shale. Units with alternating siltstones, sandstones, and shales are locally found within these sequences. The most common structures found include wave ripples, interference ripples, bedding with alternating crossbeds and horizontal or wavy bedding, trough crossbeds, megaripples, etc. In the Zigal'gin suite and Lemezín subsuite the sediments have a number of specific features: a mature mineral composition, moderate to good sorting and rounding, polycyclical quartz, and a highly mature heavy mineral fraction. All of these features are known to indicate that the sediments formed from material that had undergone extensive chemical weathering on the continent, in a humid climate, as well as considerable erosion and reworking in the depositional basin [15, 22, 44]. This suggests that the tectonic regime here during the deposition of nonquartzose sands was quite stable.

The offshore terrigenous marine assemblage is represented by two lithotypes. The first is fine-grained terrigenous sediments: clay shales and silt shales, argillites, and fine-grained clayey siltstones with thin horizontal laminations or a massive appearance (see Fig. 3 and 4). In the upper Riphean they are mainly green or gray, but darker in the lower and middle Riphean, where they are enriched in organic matter and contain carbonaceous shale (upper part of the Aisk suite, Makarov subsuite of the Bakal' suite, and some units within the Bol'sheinzer, Zigazino-Komarovsk, and Avzyan suites). Terrigenous interbeds, as well as shallow marine chemogenic and phytogenic carbonates, are characteristic of this lithotype.

The second type consists of units of massive, structureless sands with a bimodal grain size distribution, interbedded with dark shales. They are presumably formed by gravity flows and are characteristic of the lower and middle parts of the lower Riphean Bol'sheinzer suite [32]. Higher in the section this lithotype changes to a predominantly shallow-water terrigenous-carbonate deposit [34].

Carbonate deposits of the Riphean stratotype, as we have shown in previous studies, also form a number of specific, distinct assemblages of various origins.

The nearshore, very shallow water carbonate assemblage consists of limestones with horizontal bedding, crossbedding, wavy bedding, flaser bedding, desiccation cracks, and a con-

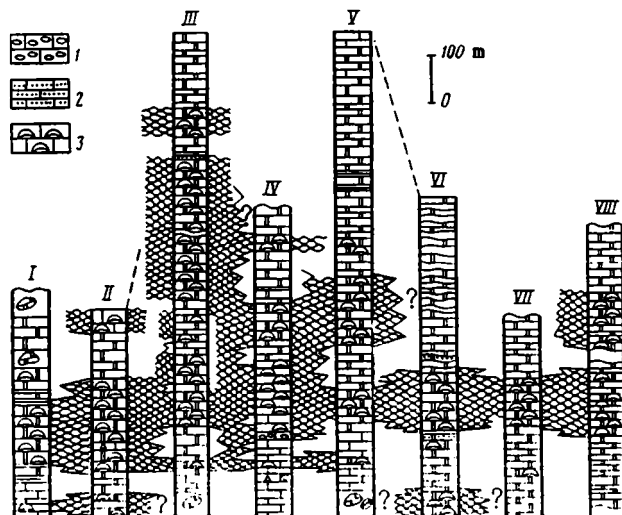


Fig. 6. Typical sections of the upper Riphean Min'yar level, composed of chemogenic marine and shallow marine carbonates. 1) Limestones with microphytoliths; 2) stromatolitic dolomites; 3) dolomites with minor terrigenous material. See Fig. 2-5 for other lithologic symbols. Sections: I) B'yanka siding, II) Minka region (from E. M. Khabarov), III) Vyazovaya, IV) Yuryuzan' reservoir, V) Bolshoi Inzer River (from E. Z. Gareev), VI) Kuzhai Creek, VII) Kal'tyagau Creek, VIII) Bugundy Creek.

siderable amount of pelitic and silty terrigenous material. Such carbonate units appear in a number of sections of the Min'yar and Avzyan suites. In the lower Satkin and lower Avzyan levels, this assemblage is represented by a sequence of platy dolomites with numerous flat-fragment breccias that succeed one another for thicknesses of 0.5-1.5 m, and alternating shale beds or fine-grained siltstones and dolomites (limestones) that contain interbeds of flat-fragment carbonate breccias. Dolomites with terrigenous material in the upper part of the Satkin suite, discovered by Yu. S. Glyzin et al. (1977) in cores from the Satkin ore field, apparently belong to this assemblage as well. Just as in the case of very shallow water terrigenous deposits, sediments of this assemblage represent a system of shoals, banks, islands, and adjacent extremely shallow flats. Deposits of this assemblage are closely associated with carbonate sediments of shallow and exposed parts of the basin.

The shallow marine carbonate assemblage consists of two lithotypes. The first is variegated, thin-bedded clayey limestone and marl (locally with interbeds of cherry-red shales). Sedimentary structures suggest a mainly shallow-water, somewhat mobile environment: In addition to horizontally bedded rocks, limestones and marls with wavy bedding and small-scale crossbedding, with interbeds of flat-fragment carbonate breccia, are found here [33]. The indication in the literature that marls with pseudomorphs of halite are present [19, 42, etc.] suggests that certain areas within the basin may have occasionally been exposed. These deposits formed in a relatively stable tectonic environment. They are characteristic in the stratotype only in the middle of the Karatau series, the Katava level (Fig. 5). Lithologic and geochemical data suggest that these deposits formed in a nearly arid climate [35] and a basin with a certain amount of fresh water [26]. A study of lateral and vertical transitions demonstrates their association, on the one hand, with shallow marine terrigenous deposits, and on the other hand, with strictly marine carbonate sediments.

The second type of shallow water carbonates, limestone with various kinds of ripples, wavy bedding, and small scale crossbedding, is found in a number of sections of the Avzyan suite and Podinzer beds.

Some levels of the Riphean stratotype are characterized by widespread development of stromatolitic (and microphytolitic) carbonates [24, 25, 36, 51, etc.], which form the shallow marine, mainly phytogenic, carbonate assemblage. This assemblage consists of limestones, dolomitic limestones, and dolomites with layered, nodular, and columnar stromatolites and closely associated chemogenic and fragmental carbonates. This assemblage is most abundant

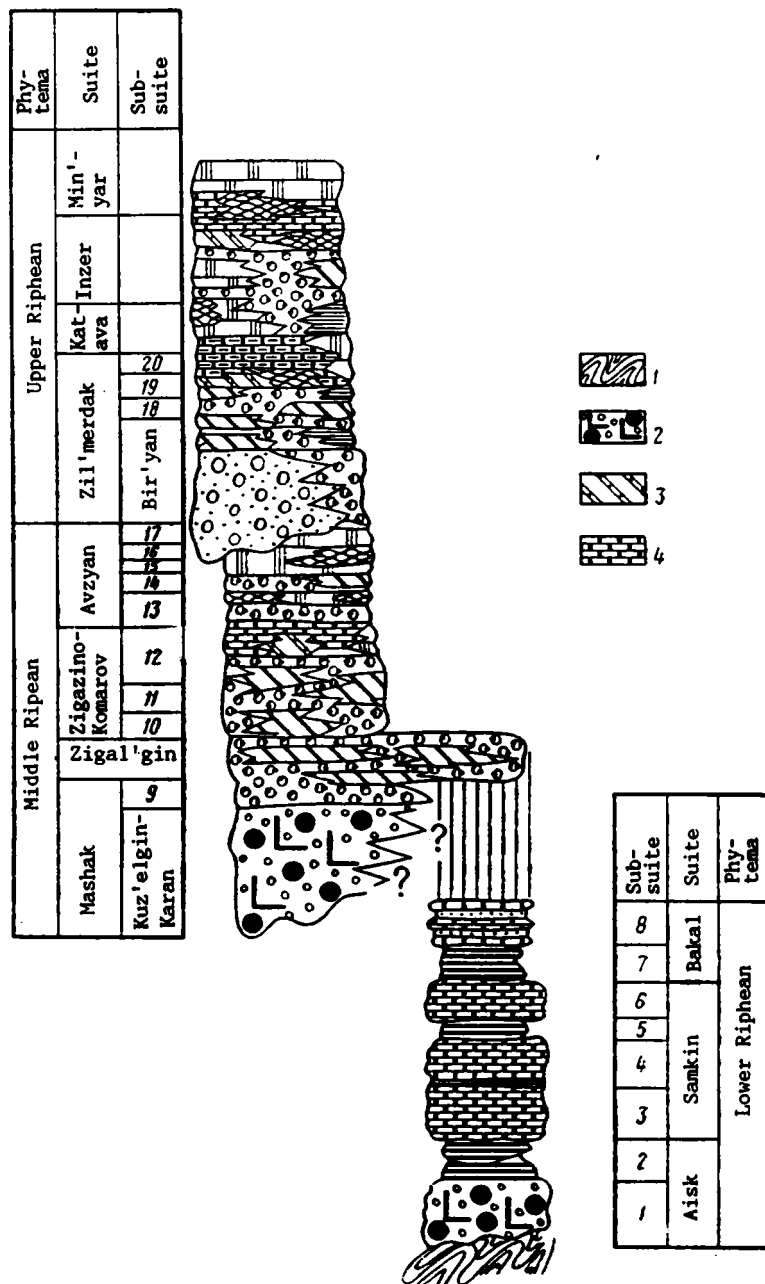


Fig. 7. Vertical succession of assemblages of various origins in the Riphean stratotype, Bashkirian meganticlinorium. 1) Highly faulted and metamorphosed Archean to lower Proterozoic rocks of the Taratash massif; 2) volcanic-terrigenous rocks, mainly continental; 3) very shallow-water carbonates; 4) shallow marine carbonates. See Fig. 2-6 for other lithologic symbols. Numbers on columns indicate subsuits: 1) Navysh, Lipov, and Chudin; 2) Kisegan and Sungur; 3) lower Nekusin; 4) upper Nekusin; 5) Polovinkin; 6) lower and upper Nesatkin; 7) Makarov; 8) upper Bakal'; 9) Shakitar and Yamantau; 10) Seregin; 11) Ambar; 12) Tukan; 13) Kataskin; 14) Maloinzer; 15) Ushakov; 16) Kutkur; 17) Revet; 18) Nugush; 19) Lemez; 20) Bederyshin.

in the Karatau series, where stromatolite sequences 150-300 m thick can be seen in the Min'yar and Podinzer levels (Fig. 6). Stromatolitic carbonates in the Yurmatin series are characteristic of certain units in the Avzyan suite, while in the lower Riphean they occur at the base of the upper part of the lower Kusin subsuite of the Satkin suite and in some units in the Bakal' suite [24, 25, 51, etc.]. Compared with the upper Riphean, however, the stromatolitic rocks in the lower levels of the stratotype make up no more than 5-10% of the carbonate units

and have more value in correlation than the stable environment of deposition suggests. In this connection, we consider that this assemblage is characteristic in the stratotype only for Karataviya.

The upper Riphean phytogenic carbonate deposits can be conditionally subdivided into two varieties. The first includes phytogenic carbonates of the upper part of the Katava suite, the so-called algal limestone with *Malginella* structures, which formed widespread algal mats. The second variety is limestone and dolomite with columnar and nodular stromatolites, which form loaf-shaped and lenticular bioherms of various sizes within platy chemo-genic carbonates in the Min'yar and Katava suites and the Podinzer beds [24, 25, 33]. Data in [54] suggest that the maximum development of stromatolitic dolomite during Min'yar time, which is found in the western and northwestern part of the present Bashkirian meganticlinorium, took place on the edge of the shallow marine shelf. Lithologic and geochemical reconstruction shows that phytoliths in the upper Riphean formed mainly in shallow marine waters [19, 26, 35].

The marine carbonate assemblage includes limestones and dolomites deposited far offshore, in the open part of the basin; they are characterized by thin horizontal or massive beds and a lack of terrigenous material. A study of the distribution of strontium in Riphean carbonates of the southern Urals [4] has shown that apparently no sedimentary dolomites formed by active evaporation are present in the stratotype, but that most of the dolomites were formed by diagenetic and catagenic alteration of calcite in marine or freshwater environments. Inasmuch as most of the original texture of the calcitic sediment is preserved during dolomitization [4], it is likely that in addition to limestones, thick primary dolomite sequences were formed in the open parts of the basin as well. This assemblage is found in the Satkin, upper Avzyan, Katava, Podinzer, and upper Min'yar levels of the Bashkirian structure.

A columnar section of the assemblages described above (Fig. 7) illustrates the main features of the Riphean sedimentary succession on the western slopes of the southern Urals.

Rift, depression, and shelf stages can be seen in the evolution of the early Riphean basin. The rift stage contains the volcanic-terrigenous, mostly continental assemblage, which is characteristic of the lower three subsuits of the Aisk suite. The combination in one locality of different, often contrasting, facies; the irregular subsidence of the basement and resulting variations in thickness and composition of the sediments from section to section; the association of trachybasalts and coarse clastic terrigenous sediments; the frequent interruptions of the section by conglomerate beds or local erosion surfaces; the "point source" of supply and short transport distance of the clastics: All of these are characteristic of the beginning of Aisk time, an epoch of rapid and irregular subsidence of the basin floor with the formation of small graben-like features in which large amounts of clastic and volcanic material rapidly accumulated.

The end of Aisk time (corresponding to the deposition of the Kisezan and Sungur subsuits) was marked by the formation of assemblages of other origins. Along the southern margin of the Taratash massif, a sandstone and conglomerate sequence of the Chudin subsuite of the Aisk suite is succeeded, after a thin transition unit, by a 700-800 m sequence of carbonaceous, horizontally laminated shales with sparse siltstone interbeds. Bedding is difficult to discern, being indicated in places only by millimeter-scale alternations of gray and dark-gray laminae. The composition, texture, and structures of the rocks in the Kusegan-Sungur level indicate that they are marine [31, 37] and were formed offshore where the bottom sediments were low in oxygen; they formed a unique unit that is an indicator of a deep trough environment. Satkin-Bakal' time was a lengthy epoch of sedimentation and the formation of a shallow marine basin with a system of synsedimentary uplifts and downwarps. The relatively small size of this basin is indicated by repeated changes in the direction of sediment supply both in the northeastern region of the meganticlinorium and in the central area [10, 23, 37, 48]. The presence of terrigenous material in dolomites of the upper Satkin suite, as well as littoral facies in the Bakal' suite [23], also support this interpretation. Slightly carbonaceous fine-grained terrigenous sediments in the lower Baikals' suite probably accumulated in local depressions on the shelf.

A reorganization of the structural style of the region took place at the early-middle Riphean boundary. This is indicated by the erosional unconformity between the Mashak suite at Yurmatina and the underlying lower Riphean deposits in the central part of the megantic-

linorium, and the truncation of terrigenous and carbonate units of the Bakal' suite by sandstones of the overlying Zigal'gin suite in the northeast part of the Bashkirian uplift. Just as in the early Riphean, the middle Riphean basin was begun with formation of a thick assemblage of volcanic and terrigenous, mainly continental and nearshore deposits. As noted above, recent studies have shown that the volcanic rocks of the Mashak suite formed an alkaline bimodal rhyolite-basalt association, which a number of petrologic and geochemical studies suggest is similar to fissure-type rift associations [8, 17, 18, 27, 41, 43]. The Mashak suite, in the center of the meganticlinorium region, contains many interbeds of basalt, sedimentary rocks, and volcanics, as well as beds and lenses of conglomerate and relatively thin but persistent units of carbonaceous shale and siltstone. The beginning of Mashak time apparently corresponds to the appearance of a system of rift-like troughs and basins in lower Riphean rocks; as in the beginning of Aisk time, it corresponds to the rifting stage of evolution of the middle Riphean. The formation of a thick assemblage of continental and nearshore sediments at this time, along with the structural reorganization of the region at the early-middle Riphean boundary, indicates a sharp change in the general style of development of the basin.

The principal source of clastic sediments in Mashak time was the underlying early Riphean deposits, and also Mashak volcanics, fragments of which are found among the pebbles in conglomerates [43, 49]. Crossbedding indicates that the supply was mainly from the west. Significant changes at the early-middle Riphean boundary apparently led to not only a different type of basin, but also to the appearance of a very unusual assemblage of deposits in the Yurmatin series. Unlike the early Riphean, the middle Riphean basin formed a volcanic-terrigenous assemblage followed by a long period that may be called an epoch of slow transgression, marking the end of the Mashak time and corresponding to Zigal'gin and Zigazino-Komarov time [34]. The textures and structures of the sandstones and siltstones in the upper part of the Mashak and Zigal'gin suites indicate the predominance of shallow to very shallow water and the deposition of variegated sediments in wave and current zones, and the formation of bars and spits with periodic exposure of shallow-water flats. In this environment, clayey and silty sediments with organic matter were locally deposited in very shallow areas.

On the whole, deposits at this level were formed during relatively stable tectonic conditions and were affected by the erosion of areas of intensive chemical weathering in a humid climate. Turning to sedimentation in the overlying Zigazino-Komarov suite, we see a complex terrigenous sequence that is enriched to some degree in organic matter and that includes both shallow- and very shallow-water deposits [34]. These deposits are very erratic and are apparently represented throughout the basin by a complex mosaic of periodically exposed and shallow marine zones in a discontinuous expanse. Thus the Zigazino-Komarov level, like the Zigal'gin, is a continuation of an epoch of slow transgression of the basin over a peneplain. Unlike the early Riphean, over nearly its entire extent this sedimentation took place in a very shallow basin with archipelagos of flat, low islands, banks, shoals, and rises, and is characterized by a complicated configuration of shallow and very shallow nearshore environments. Typical shallow marine deposits occur only in the middle of the middle Riphean Avzyan level. They consist of terrigenous units and sequences of interbedded stromatolitic and chemogenic carbonates. In the Kataskin subsuite of the Avzyan suite, however, there is some evidence of relatively shallow-water sediments: numerous interbeds of flat-fragment carbonate breccia in units of interbedded limestone, siltstone, and shale. Only at the beginning of the Ushkov level may we postulate the appearance of a well expressed shallow marine basin. The third (shelf) stage in the development of the middle Riphean sedimentary basin on the west slope of the southern Urals thus corresponds to terrigenous and carbonate deposits of the Ushakov, Kutkur, and Revet subsuites of the Avzyan suite, concluding the Yurmatinia section.

The middle and upper Riphean boundary in the study area is never more distinctive than between the Burzyania and Yurmatinia. It is marked by the appearance of a thick association of continental and nearshore marine clastic rocks of the Bir'yan level above shallow water, strictly marine shelf deposits.

The upper Riphean deposits of the west slope of the southern Urals, like early and middle, are quite varied: continental nearshore, very shallow to shallow marine, and fully marine sediments [33]. They differ in appearance from the early and middle, however. The upper Riphean is characterized by variegated deposits (Zil'merdak, Katava, and Inzer levels), by widely developed glauconitic sediments, and by various stromatolitic units, mainly sub-

littoral. Organic material is lacking, and most significantly, volcanic sediments as well. This is no doubt related not only to changes in climate, but also to significant changes in the depositional basins themselves.

In earlier reports we provided a detailed analysis of the lithofacies of the upper Riphean deposits of the Bashkirian meganticlinorium, and presented a description of the facies assemblages and their patterns of distribution; we also compiled a diagrammatic paleogeographic map and proposed an evolutionary model for the basin of sedimentation [29, 30, 33, etc.]. Without dwelling on the details of these results, we will consider only the main features of basin development.

In the first stage, during Bir'yan and Nugush time, thick alluvial and deltaic deposits formed on the west flank of the basin under conditions of differential compensating subsidence. The size of the shallow marine zone was considerably smaller than at the end of the middle Riphean. The boundary between the continental and coastal environments during Bir'yan time was probably somewhat west of the town of Inzer [29]. The sharp reduction in the size of the marine basin was no doubt caused by strong movements on the east flank of the Russian platform, probably with some uplift of its margin. Later, at the end of Zil'merdak time, transgression probably began rapidly, progressing from east to west and leading to the appearance of a broad, well oxygenated shallow-water basin in Katava time. Thus the trend toward regression changed to transgression at about the middle of Zil'merdak time. The maximum extent of shallow marine deposits occurred in the middle of the late Riphean, since mostly marine sediments were deposited at the end of Min'yar time [33]. It should be noted that the presence of glauconitic quartz sediments and extensive chemogenic carbonates in the upper part of the Min'yar suite, with no evidence of terrigenous material, suggests that the basin was vast in size.

* * *

Thus the evolution of the early Riphean basin involved three stages. The first, rifting, with rugged relief in the source area and volcanic-sedimentary associations that differed markedly in size and form, is characteristic only of the beginning of Aisk time. This was followed by a shelf and trough stage. The middle Riphean basin, like the early, began with deposition of a thick volcanic-terrigenous assemblage of continental and nearshore origin. Later slow transgression took place over a flat, smooth plain with deposition of terrigenous shallow and very shallow sediments. The shelf stage in the middle Riphean (as in the early and late) was not very distinct and corresponds to the end of Avzyan time. At the beginning of the late Riphean there was considerable shrinkage of the marine basin and deposition in Bir'yan time of a thick complex of alluvial and deltaic sediments, later changing to shallow and very shallow deposits and, in the middle of the late Riphean, shelf sediments. Unlike the earlier part of the late Riphean, no rift stage appeared. At this time there was a sharp change in the type and sequence of deposits from those of the lower and middle Riphean. The Karatau series, in the distribution of deposits of various origin through the section and in its specific characteristics, is very reminiscent (in both sensu stricto and, along with the Uks suite, sensu lato) of the Siberian Riphean platform and pericratonic (miogeosynclinal) sections. The late Riphean of the western slope of the southern Urals was apparently a time of transition from a rift-depression regime to a plate regime.

The distribution of assemblages of different origins in the Riphean stratotype, and comparison of their succession in the Bur'zyan, Yurmatin, and Karatau series, place in doubt the idea persisting in the literature that all three series are alike [14, 16, 21, etc.]*, and consequently also the view that the formation of the sedimentary assemblages of the early, middle, and late Riphean was the same. Actually, as shown above, basin development took place under conditions that were specific for each of these stages, which resulted in the occurrence in the stratotype of assemblages that vary in origin and sequence.

In addition to this, the investigation raised a number of new questions. The first of these is the lateral relationship of assemblages of different origin in the lower and middle Riphean levels both in the stratotype area and in the surrounding region.

*For example, in [16, p. 386] we find "...Each series constitutes a megarrhythm with a conglomerate at the base and sandstone grading up to carbonate rocks at the top..." and from Kozlov [21, p. 15], "...Series begin with poorly sorted sandstone and end with clayey and carbonate rocks."

Secondly is the nature of the changes, in the style of development of the sedimentary basin, at the boundaries between the early and middle and between the middle and upper Riphean. Related to this question, which has not as yet received a satisfactory answer, is the broader problem of selection of a typical locality for analysis of the main features of basins of different ages, since the available information indicates sharp facies variations between different stratigraphic levels, and thus a quite varied overall distribution of assemblages which contrast more toward the margins of the paleobasins and less toward their centers.

The question of the paleoclimatic and paleotectonic conditions of deposition of the assemblages of various origins described above, and the paleogeography during the formation of the so-called graben associations and of the entire basal level of the Riphean, also requires special attention.

Solution of all of these problems, along with data on a number of other methods of investigation, will provide an objective picture of the evolution of late Precambrian sedimentary basins in the area of the present western slopes of the southern Urals, and using the Riphean stratotype as a standard, and will spell out the overall conditions of formation of the basins.

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RELATIONSHIP BETWEEN GEOCHEMICAL CHARACTERISTICS OF SEDIMENTS AND ENVIRONMENT OF DEPOSITION

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Using the Middle Miocene sediments of the Cis-Caucasus as an example, we discuss the influence of physical-geographical conditions of deposition upon geochemical characteristics of sediments. We show that the use of correlation coefficients and correlation diagrams constructed on their basis permit identification of content distributions of chemical elements in sedimentary strata.

The geochemical characteristics of sedimentary rocks depend to a significant degree upon physical-geographical conditions of sediment accumulation. Among these conditions, we should include composition of distributive provinces, intensity and dominance of chemical or physical weathering, remoteness and form of transported material to the terminal basin, hydrodynamic activity of the basin, etc. Postsedimentational conversions of materials (increasing in intensity during the stage of sedimentation) play an appreciable role.

The multiplicity of factors influencing the geochemical character of sedimentary rock results in high variation of actual point contents of chemical elements. Therefore, investigations of geochemical characteristics of both recent sediments and ancient deposits are impossible without considering significant volumes of numerical data, since it is only by averaging such data that one can discover important trends in the behavior of chemical elements. The use of very simple techniques for mathematical processing of numerical data, in particular, computation of correlation coefficients, allows one to more or less objectively distinguish groups of chemical elements characterized by similar behavior, to establish the existence of interrelationships between elements, to evaluate their strength and, in the end, to distinguish types of chemical-element distributions. One should not forget, of course, that mathematical processing of geochemical information is formal in character and that the use of its results in departures from traditional lithological-facial, paleogeographical, mineralogical, and other investigations can lead to certain difficulties.

Middle Miocene sediments of the Cis-Caucasus served as the object of investigation in this report. The Middle Miocene is one of the most interesting times in geological history; this is mainly because the south of the European portion of the USSR during the Maikopian-Middle Miocene were affected by processes of tectonomagmatic activation associated with Alpine folding. Transverse structures were the primary manifestation of these structures. As a consequence, there were abrupt changes in depositional environments and also volumes of sedimentary material being supplied to the basin. One result of these movements was uplift of the Stavropol' arch, which divided the previously unified Cis-Caucasian paleobasin into three zones: eastern, central, and western, corresponding in territory to eastern, central, and western Cis-Caucasus. In area, the central zone does not measure up to the western and eastern zones. It includes the Stavropol' arch, which tended toward uplift during the Miocene, and also includes the narrow, saddle-shaped Belomechet trough. The Indol-Kuban' and the Tersk-Caspian foredeeps are the principal structural elements of the western and eastern zones (Fig. 1). They steadily subsided over the course of the Middle Miocene.

Consequences of differences in tectonic structures in the zones distinguished included differences in the volumes of sedimentary material accumulated within zones and also differences in the proportions of material supplied from the two chief sources: the Russian platform and Caucasian Island. It should also be noted that the Middle Miocene drainage network and migration of the mouth of the largest river on the Russian platform, the Paleo-Don, exerted a great influence upon the formation of lithological-facial patterns in the three zones of the basin [9].

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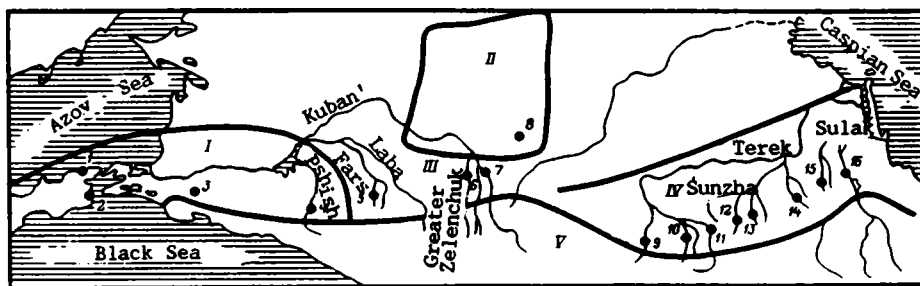


Fig. 1. Map of sections of Middle Miocene sediments. I) Indol-Kuban' trough; II) Stavropol' arch; III) Belomechet trough; IV) Tersk-Caspian trough; V) Greater Caucasus meganticlinorium; 1-16) sections [1) mouth of Lesser Kamyshlak; 2) Kop-Takil; 3) Kudak-Kiev area; 4) Pshish River; 5) Fars River; 6) Greater Zelenchuk; 7) Kuban' River; 8) Mt. Bryk; 9) Urukh River; 10) Suadag-Don River; 11) Buivolina ravine; 12) Fortanga River; 13) Malaya Roshnya River; 14) Elistanzhi River; 15) Yarysk-su River; 16) Sulak River].

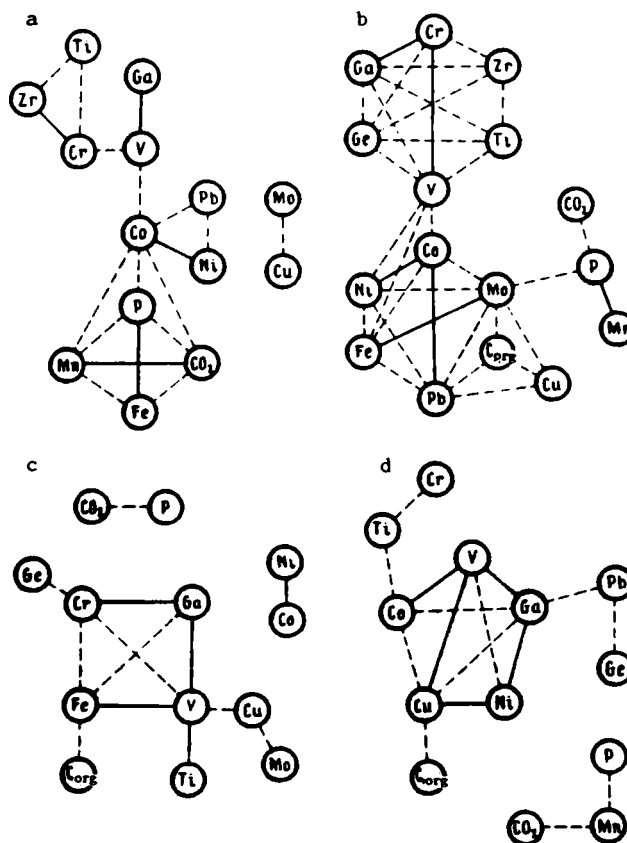


Fig. 2. Correlational diagrams of clays of eastern zone. Sections: a) Sulak River; b) Élistanzhi River; c) Buivolínaya ravine; d) Uruk River.

We studied approximately 20 sections of Middle Miocene sediments in detail; 16 of these were included in a lithological-facial profile cutting across all three zones of the paleobasin (see Fig. 1) [10, 11, 16]. On the basis of evidence gathered along the profile and numerous published data [1, 2, 4, 5, 7, 12, 17, etc.], we will briefly describe the sedimentary strata in the western, central, and eastern zones of the basin.

Sediments of various shallow-water facies primarily occur in the western zone. Only within the axial portion of the Indol-Kuban' trough is there a facies consisting of calcareous-clayey sediments associated with relatively deep-water portions of the sea. At the same time, the proportion of sandy sediments is relatively low. In the sections studied, which are located in the southern portion of the western zone, interbeds of sandstones occur

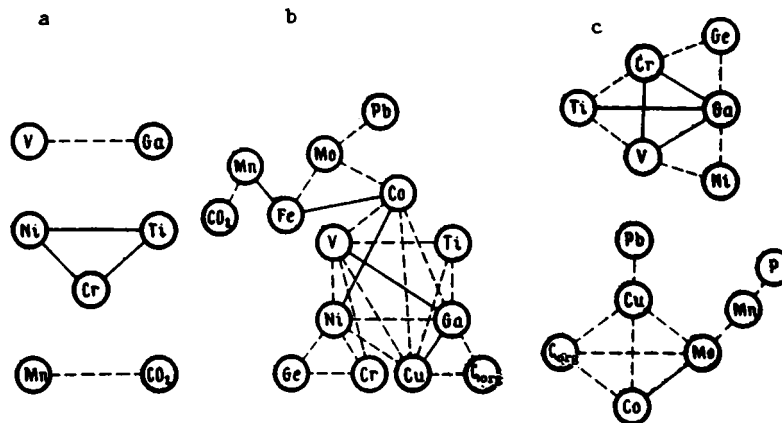


Fig. 3. Correlational diagrams of clays in the central zone. Sections:
a) Mt. Bryk; b) Kuban' River; c) Greater Zelenchuk River.

only in sections along the Fars River and in the area of the Lesser Kamyshlak. In the first case, the sandstone interbeds are traces of the activity of rivers carrying out sandy material from the Caucasian Island; in the second case, they are coastal-marine formations. As a rule, the sandstones of the Fars River are poorly sorted and contain a significant portion of clayey-silty admixture. The sandstones of Kamyshlak are so calcareous that they sometimes grade into sandy limestones. Sandy sediments are more prevalent in the northern portion of the western zone, and their portion increases significantly in the upper parts of the Karaganian and Konkian. Grey clays characterized by relatively low contents of C_{org} , high carbonate content, and a significant admixture of silty-sandy material predominate among the clays. In general, the clays and sandstones are distinguished by weakly sorted material. Thin interbeds of bryozoan, shelly-detrital, and, more rarely, pelitomorphous limestones and stromatolithic formations are widely occurring in sections of the western zone. Extended marker horizons are absent in the deposits of the western part of the profile, and the lateral lithological-facial variability is appreciable. Diagenetic conversions are weakly manifest; this is reflected in a insignificant quantity of interbeds of carbonate concretions and in an absence of macroscopically detectable sulfide nodules.

In the central zone of the basin, sediments of the Stavropol' arch can be fairly easily distinguished from the strata of the Belomechet trough. Sandy sediments of facies of moving and strongly moving shallow water predominate in the Stavropol' arch (the section at Mt. Bryk). Here, under shallow-water conditions, growth of local rises, and a general tendency toward uplift of the anticline, the sediments were repeatedly subjected to washout and reworking. The maximum number of washouts and the maximum lateral variability of sediments within the profile occur in this section. In the Belomechet trough, sandy rocks are concentrated in the lower portion of the Chokrakian. Above, at the top of the Chokrakian and in the Karaganian, clays, and, to a lesser degree, siltstones predominate. The clays are primarily grey, i.e., contain a significant silty admixture, and are poor in organic matter. Postsedimentational conversions are weakly manifest in the sections of the central zone. In the section along the Greater Zelenchuk, there are a few interbeds of carbonate concretions and sparse, small shot-like sulfide concretions; in the section along the Kuban' River, there are only isolated carbonate concretions; on Mt. Bryk, neither carbonate nor sulfide concretions have been found.

The lithological-facial map of the eastern zone of the basin is most interesting. Its characteristic feature is an interbedding of a facies consisting of silty-clayey rocks of a relatively deep-water area of the sea and sandy sediments of bottom currents, i.e., a normal lateral facial zonation in which the granularity of the sediments regularly decreases from the margin to the axial portion of the basin and is periodically and abruptly disrupted by the widespread occurrence of sandy sediments over a large area of the basin, including its axial, most subsided portion. Quartz oligomictic sandstones form interbeds a few meters to a few tens of meters in thickness in sections of the eastern portion of the profile and are good markers, extending for tens and even hundreds of kilometers. Some textural features (cross-bedding, graded bedding, clay balls at the bottoms of interbeds, etc.) allow us to infer a bottom-current origin for the sandstones. Thin, poorly sorted sandstones of coastal-

of interbedded sandstones and clays in the eastern Cis-Caucasus was a result of this two-pass mechanism supplying sedimentary material during Chokrakian-karaganian times. Thus, the sediments in the eastern zone primarily formed as a result of mature, past, intensive chemical weathering of material from the Russian platform which was fed to a terminal basin in the vicinity of present-day northern Caspia via waters of the Paleo-Don and then dispersed by current over the entire basin.

The Central Zone. The peculiar nature of the stratum accumulated in the central zone of the basin was controlled by the steady tendency of the Stavropol' arch toward uplift. A shallow sea with numerous islands and shoals existed within it during the entire Middle Miocene. Supplies of sedimentary material to this portion of the basin were small; this is reflected in the small thicknesses of sediments accumulated. Only at the beginning of Middle Miocene times (during the first half of the Chokrakian) were significant volumes of detrital material carried away from the Russian platform, as a result of regression and significant lowering of the base level of erosion within the central Cis-Caucasus; the Paleo-Don transported the material and became the largest river of the Russian platform not long afterward [8]. The supply of material from the platform sharply reduced after migration of the mouth portion of the Paleo-Don toward the East [9]. It should be noted that sedimentation within the Stavropol' arch proceeded primarily as a result of washout erosion of growing islands and shoals, i.e., as a result of washout of strata accumulated during the Chokrakian and also as a result of supply of suspended matter by currents from the eastern zone. The influence of Caucasian Island, as in the eastern zone, was minor and the southern Stavropol' swell, the elevation of which served as an obstacle to transport of suspended matter, became even less pronounced. The situation was somewhat different in the Belomechet trough. Here, as on the anticline, a fairly thick sandy-clayey packet accumulated during the early Chokrakian. Subsequently, sedimentation was controlled by supplies of suspended matter from washed out structures of the Stavropol' arch and from the eastern zone. The influence of Caucasus material here was undoubtedly stronger than on the anticline, but apparently manifested only near the inflow of rivers from Caucasian Island emptying into the basin. Thus, the channel remains of a small river [3] occur in the Chokrakian sediments of the Kuban' River; this means that the influence of the Caucasus should be detectable in the Kuban' section. So, despite certain differences in conditions of deposition on the Stavropol' arch and in the Belomechet trough, the composition of the sedimentary stratum was controlled by material from the Russian platform and, only episodically, from Caucasian Island.

The Western Zone. Sedimentation in this zone occurred to an approximately equal degree because of Caucasian Island and the Russian platform. Material was contributed by several small rivers. On the northern shore, traces of such rivers occur in the vicinity of the Donets prominence [6] and the detrital cone of a fairly large river in the Kuzhor-Laba interfluvium is clearly identifiable in the southern portion of the zone. At the end of Karaganian times, moreover, the sedimentary material in the western zone was supplied from the Paleo-Don platform, altering the position of the mouth portion of the river. The supplies of material were, however, short-term; secondly, they apparently did not measure up to supplies to the central and eastern zones in terms of intensities and volumes of material; this was a consequence of a general quieting of tectonic activity in the western zone. The weak hydrodynamic activity in the western zone of the basin resulted in platform material predominating in the northern portion of the zone and Caucasus-derived material predominating in its southern portion. Thus, despite the warm and moist climate characterizing Caucasian Island during the Middle Miocene, active uplift and the denudation of the Caucasus did not permit chemical weathering processes to progress very far. So, sedimentation in this zone was characterized by most tranquil depositional environment in the basin as a whole, lack of one sharply predominating source of material, and lacking a single predominating area supplying material to the basin.

Thus, the physical-geographical depositional environments of the sedimentary strata in the three identified zones of the basin can be distinguished fairly easily. The differences are clearly manifest in the lithological-facial characteristics of the western, central, and eastern strata. We will now discuss several peculiar conditions of sedimentation which show up in the geochemical characteristics of the sediments.

The principal types of rocks in the sections investigated and clays and sandstones, which, on the average, constitute 80 and 12% respectively of the total thickness of sediments. The material compositions of these types of rocks differ fairly sharply; results of the analyses for clays and sandstones were therefore processed separately. In all, approximately

500 samples of clays and approximately 200 samples of sandstones were analyzed from the 16 sections studied in detail. Contents of V, Cr, Ni, Co, Pb, Cu, Ga, Ge, Mo, CO₂, C_{org}, Fe, Mn, P, Ti, and Zr were measured chemically and by quantitative spectral analysis. Statistical calculations, of correlation coefficients in particular, were then carried out.

The results of calculations of correlation coefficients are shown in graph form for better visibility (Figs. 2-5). Here, the five-six strongest relationships are indicated by solid lines and the remaining significant relationships (at the 5% level of significance) are indicated by dashed lines. First, we will consider results from calculating correlation coefficients for chemical elements in clays. For the eastern zone, correlational diagrams (Fig. 2) are shown for the Uruk, Buivolina, Elistan, and Sulak rivers, each of which characterizes one of the structural-facial subzones of the eastern Cis-Caucasus which we have identified [16]. Three groups of elements are fairly clearly segregated in the two eastern sections of the eastern zone (the Elistan and Sulak rivers). The first group includes V, Cr, Ti, Zr, Ga, and Ge; the second group includes Co, Ni, Pb, Mo, Cu and Fe; the third group includes Mn, P, and CO₂. In the western sections of the eastern zone, however, this pattern weakens somewhat. Thus, only the first group can be fairly clearly distinguished along the Buivolina Ravine, and the link between elements of the second group declines significantly in this area. Finally, in the Uruk River section (the most western section in the eastern zone) separation of elements into the first and second groups is almost entirely absent.

Using the Black Sea as an example, Strakhov [15] previously showed that the distribution of chemical elements in the superficial layer of sediments was primarily due to the manner of migration of chemical elements in stream flow and subsequent mechanical differentiation of the sedimentary material in the basin. He identified a group of geochemically slightly mobile elements (Ti, Zr, Ge, Cr, V, Ga, and TR) primarily migrating along with the suspension and bound with the silt fraction in the sediment and also identified a group of more geochemically mobile elements (Fe, Mn, Ni, Cu, Co, Mo, W, As, Se, P, Ca, CO₃), for which migration is significantly linked to gravitation of soluble forms toward the pelitic fraction in the sediment.

A comparison of the groups of chemical elements identifiable on the basis of correlational diagrams with those presented in [15] shows that the first group is composed of geochemically weakly mobile elements, while the second and third are composed of more geochemically mobile ones. In other words, the classification of chemical elements into groups on the basis of correlations conforms fairly well to the physical-geographical conditions associated with the formation of the sedimentary stratum in the eastern zone. Mature platform material subjected into intensive chemical weathering predominates in the Sulak and Elistan sections. Over the course of prolonged removal and transport of material from the platform to the terminal basin, separation of elements into groups of geochemically weakly mobile elements, elements moving with suspensions, and more mobile elements (a portion of which travelled in the form of true or colloidal solutions) took place. This differentiation of elements into groups was maintained during sedimentation; this is clearly evident on the correlational diagrams. The lack of separation of elements into groups in the Uruk River section (see Fig. 2) is also in good agreement with the conditions of sedimentation. On the other hand, this section is located at a maximum distance (for the eastern zone) from the mouth of the Paleo-Don, i.e., from the principal source of mature, well differentiated sedimentary material and, on the other hand, lies near the remains of Caucasian Island (its central most-actively-rising and thus washed-out portion). In this region where sedimentation proceeded under coastal-marine conditions, the volume of material arriving from the Caucasus apparently exceeded the supply of material from the platform. This makes the lack of separation of elements into groups understandable, since rapid denudation and a short route to the site of sedimentation did not allow differentiation of elements. The section located to the east of the Uruk River, along the Buivolina ravine, occupies an intermediate position. The correlational diagram shows, though not very clearly, that the first group of chemical elements is segregated here, i.e., the influence of platform material was decisive, even in this section located near Caucasian Island.

It is impossible not to notice that postsedimentational conversions had an influence on the correlational connections between elements. Primarily, this is the case for the geochemically more mobile elements, or elements of the second group according to Strakhov [15]. In the Middle Miocene stratum, where diagenetic processes are fairly active, these elements

make up the second and third groups, groups which were segregated as a result of diagenetic sulfide- and carbonate-formation, and more to the point, a redistribution of chemical elements over the course of these processes. High contents of such elements as Ni, Co, Pb, and Cu [16], i.e., elements of the second group, are associated with sulfide (usually pyritic) concretions. Previously, we made quantitative estimates of sulfide and carbonate concretions and interbeds in Middle Miocene sections [16] which showed that maximum quantities of diagenetic sulfides occur in the Elestanzhi section. Apparently, the second group of elements is very clearly distinguishable on the correlational diagram of the Elestanzhi section precisely because of sulfide formation. While the increase in correlation between the elements of the second group was due to sulfide formation, the redistribution of carbonates resulted in segregation and close relationships between Mn, P, and CO_2 , i.e., between elements of the third group.

In the central zone of the basin, correlation coefficients were computed for three sections (see Fig. 3). Significant correlations were seldom found in the Mt. Bryk section, and all of them are associated with elements of the first group. A pattern similar to that in the eastern zone occurs in the section along the Greater Zelenchuk River, i.e., a fairly clear segregation of the first and second groups of elements. Finally, the elements of the first and second groups in the Kuban' River section are fairly closely correlated with one another, i.e., they did not separate. The elements of the third group are more or less clearly segregated in all three sections.

It is easy to see that the characteristics of sedimentation in the central zone left their mark on the correlations between elements. As in the eastern zone, material from the Russian platform predominate here; hence separation of elements into groups took place. This can be seen in the Mt. Bryk and Greater Zelenchuk River sections. Uplift of the Stavropol' arch resulted in washout erosion of the stratum accumulated during the early Chokrakian and mixing of this material with terrigenous material again arriving primarily from the eastern zone of the sea. Thus, there were actually two sources of material during accumulation of the stratum in the Mt. Bryk section, although all of the sedimentary material arrived from the Russian platform in the final analysis. The results of such transport of sedimentary material included a general weakening of correlations between elements and their maintenance only for certain representatives of the first group. The weakness of the diagenetic conversions in the sediments of the Stavropol' arch, expressed in the almost complete lack of macroscopically visible sulfide concretions and the minor occurrence of carbonate concretions, was reflected in the lack of correlations between elements of the second group. Material released primarily during washout erosion of islands and shoals on the Stavropol' arch, i.e., well differential platform material was involved in the accumulation of the Middle Miocene stratum of the Zelenchuk section located in the Belomechet trough; this led to segregation of elements of the first group. In the central zone, the strongest development of diagenetic processes (in the sediments of the Zelenchuk section) was due to the presence of correlations between elements of the second group.

The peculiar nature of the correlational diagram of the Kuban' section, expressed in the lack of segregation of elements of the first and second groups, can be explained by the strong local influence of Caucasus material arriving by a river which left traces in the vicinity of the Yaman-Dzhalga ravine [3]. In the western zone of the basin, there are five sections for which we computed correlation coefficients of clays (see Fig. 4). The correlational diagrams of these sections differ sharply from those discussed above in that there is no separation of groups within one of them and in that the strongest correlations frequently occur between elements of different groups. Elements of the third group are segregated only within the Kudak-Kiev area and, to a lesser degree, in the Kop-Takil and Fars sections. The abrupt changes in the character of correlations can be explained by a change in sources of supply. In the western zone, the contributions of platform and Caucasus materials are approximately equivalent. The lack of active hydrodynamic activity and the along-the-coast direction of existing currents results in a predominance of platform material in the northern portion of the western zone and a predominance of Caucasus material supplied to the southern portion. Taking into account that the sections studied are located in the southern portion of the western zone, it becomes apparent that the lack of separation of elements into groups is due to the weak differentiation of material supplied from Caucasian Island.

Computations of correlation coefficients in the sandy sediments of the Middle Miocene showed that similar correlational diagrams, on which there is no clear separation of elements into groups, are obtained for all three zones of the basin (Fig. 5). However, differences

in the physical-geographical conditions of formation associated with the western and eastern strata are reflected in the correlational diagrams of the sandstones. In the eastern and central zones, the strongest correlations occur between elements of the first group, while in the western zone, they occur between elements of both the first and second groups, i.e., a definite segregation of elements of the first and second groups actually occurs in the east and in the center, as in the case of clays. In the west, there is no segregation. Moreover, there is a larger number of significant correlations (again principally between elements of the first group) than in the western sections when a switch is made from a 5% to a 0.1% level of significance. In other words, the correlational diagrams of the sandstones, like those of the clays, show high degrees of maturity and sorting in the eastern and central zones relative to those in the western zone, i.e., indicate a platform origin for the first and a Caucasus origin for the second.

Thus, the calculations of correlation coefficients and the use of correlational diagrams allows us to fairly reliably identify groups of chemical elements and, in the final analysis, to evaluate the influence of conditions of sedimentation upon the behavior of chemical elements in sedimentary strata.

While characterizing the distribution of elements in the Upper Paleozoic humid sediments of the USSR [13, 14], Strakhov showed that all of the identified types of distributions and their modifications form a single geochemical series, a series of geochemical mobility of elements at the stage of sedimentation, reflecting the changing physical-geographical conditions. Strakhov proposed the ideal geochemical profile method for identifying certain types of distributions. This method is based upon comparative examination of the distribution of elements in the rock series sandstone-siltstone-clay-marl-limestone, i.e., a generalized ideal profile from the coastal to the pelagic zone.

Using the ideal geochemical profile method, we demonstrated that the distributions of chemical elements in the Middle Miocene sediments of all three zones of the basin belong to three different modifications of an ordered type [11]. Thus, differences in physical-geographical conditions resulted in different types of distributions of chemical elements within different zones of a single basin.

At the same time, the correlation coefficient characterizing correlations between elements and establishing separation of elements into groups also characterizes, in the final analysis, the degree of geochemical mobility of elements in one or another environment. In other words, appropriate correlational diagrams can be linked to certain physical-geographical conditions, and hence types of distributions of elements, i.e., use of correlation mobilities of elements from characteristic correlational diagrams and allows us to distinguish types of elemental distributions.

Examination of correlational diagrams based on all three zones of the Middle Miocene basin allows us to distinguish three of distributions of chemical elements corresponding to different modifications of the ordered type of distribution suggested by Strakhov. These include: an eastern type, where separation of elements into groups took place; secondly, a western type, where such separation did not take place; a transitional or central type, where separation into groups is not clearly expressed.

On the basis of existing data, we unfortunately cannot construct a whole series of correlational diagrams analogous to the series constructed by Strakhov, but it is fairly obvious that a variegated type of distribution should be characterized by a lack of separation of elements into groups according to degree of mobility, inheritance of significant correlations from parental rocks, and weakening or complete absence of significant correlation when there were several equivalent sources of sedimentary material possessing different geochemical features.

Thus, the use of correlation coefficients and the construction of correlational diagrams, together with lithological-facial and paleogeographical analyses make it possible to typify distributions of chemical elements in sedimentary strata. An advantage of the statistical method over the ideal geochemical profile method is the possibility of using only one lithological variety of rock, just clay, instead of a rock series from sandstones to limestones.

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GEOLOGIC-LITHOLOGIC FORMATION SETTINGS OF LEAD-ZINC DEPOSITS IN PLATFORM COVERS

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UDC 553.447

Distribution patterns of lead-zinc ore deposits in platform cover beds are discussed. The role of the various factors in the formation of these deposits is analyzed: the proximity of oil/gas basins and evaporitic sediments, the presence of long-lived faults, and the development of pre-ore dolomitization in ore-enclosing terrigenous-carbonaceous beds.

Many large lead-zinc deposits are known to be located in the covers of Precambrian and younger platforms. Examples include the Midcontinent deposits of the well-explored Upper Mississippi, southeastern Missouri, the Tri-State and other areas (United States), Pine Point (Canada), Upper Silesia (Poland), Taynagh, Silvermines, and others (Ireland), Sardan and Tabornoe (USSR), and others.

The geology and genesis of deposits of this type have been discussed in many publications which have appeared in recent years [8, 11, 20, 21, 22, 27, 29, 31]. These authors arrived at different conclusions on the key issues of the origin of ores in these deposits. In the present paper we attempt to discuss these problems for lead-zinc deposits localized in carbonate rocks of the covers of Precambrian and Paleozoic platforms in the light of the latest data.

The deposits of this group are classified by their geologic and commercial characteristics as stratiform lead-zinc placers located mainly in lime-dolomite sediments and characterized by certain geologic and mineralogic features:

- ore bodies are situated in carbonate rocks that have experienced epigenetic dolomitization and less often quartzified sandstones;
- they are represented mainly by stratal and lenslike bodies mostly occurring conformably in the surrounding rocks;
- the prevalent ore textures are of veinlike and veinlike-inset type;
- magmatic rocks, except for rare dikes of basic composition, are usually absent near the deposits;
- the mineral composition of the ores is simple: the principal ore minerals are sphalerite and galena, with carbonate, quartz, and barite as vein minerals.

Iron sulfides (pyrite, marcasite, pyrrhotite, etc.) are found in minor amounts. The quantitative proportions between sphalerite and galena vary widely, so that the ores can be classified for practical purposes as high-zinc, high-lead, or lead-zinc.

Previous investigators have noted that most ore deposits and ore shows of this type on platforms are located near crystalline shields or ancient basement protrusions. In particular, deposits in southeastern Missouri and the Tri-State area are located close to the Ozark dome, whose core is made up of Precambrian rocks. Mineralization in the Pine Point area is confined to the margin of the Canadian Shield. The deposits in Upper Silesia are situated near the Czech crystalline massif. The Sardan and Tabornoe deposits are located in the direct vicinity of outcrops of the Siberian Platform basement. This pattern is also clearly traceable in the East European Platform. The high-lead Laisval and Vassbo deposits are situated on the northwestern extremity of the Baltic Shield. Numerous lead-zinc ore shows are located on the western margin of this shield (in Estonia and Latvia). The proven lead-zinc ore shows of the central East European Platform are situated on both sides of the Voronezh massif: the Mikhailov ore show zone in the southwest [2] and the Voronezh zone in the northeast.

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Fig. 1. Distribution of lead-zinc ore fields and oil deposits in geologic structures of the Midcontinent Plate and the Appalachians (data of V. E. Khain, V. V. Popov, and F. G. Snider): 1) Prepaleozoic basement; 2, 3) sedimentary cover (2-Epihercynian platforms, 3-young platform); 4) boundaries of sedimentation basins (synclises); 5) axial lines of anticlises; 6) piedmont foredeep sediments; 7) arch rises (A-Wisconsin, B-Ozark); 8) Caledonian-Hercynian folded zones; 9) metalliferous districts with stratiform lead-zinc deposits (1-upper Mississippi Valley, 2-Tri-State, 3-southeastern Missouri, 4-Illinois-Kentucky, 5-Jefferson City, 6-Austinville-Ivanhoe); 10) oil/gas fields; 11) faults (I-Namaha, II-Kentucky-Missouri).

The lead-zinc ore shows of the Donetsk Basin are localized within the Donetsk-Dnieper aulacogene, surrounded on both sides by ancient uplands. Finally, the lead-zinc ore shows of the Dniester area (Podol, Volyn, etc.) lie close to the southern margin of the Ukrainian crystalline massif [5].

Deposits of a platformal cover close to lead-zinc mineralization sites are typically slightly dislocated. They mostly form gentle folds with wing-tip angles of a few degrees. However, disjunctive faults including deep disruptions are also quite common. Two types of these forms bear mentioning: faults conforming to the boundaries of shields and massifs, and series of large deep faults often crossing several platformal structures. The former are exemplified by the Podol fault zone in the Dnieper region and the latter by the sublatitudinal Midcontinent faults in the United States (see Fig. 1).

The genetic causes of the location of lead-zinc deposits close to the margins of shields and crystalline massifs can vary. Some investigators, postulating a sedimentary origin of stratiform lead-zinc deposits [1, 7], see shields and crystalline massifs as the provenance source of the lead and zinc found in ore shows in the zones of disseminated sulfidic mineralization in Precambrian metamorphosed rocks. The sources of lead and zinc during erosion of Precambrian structures can include not only sulfides that form ore shows and disseminated insets but also rock-forming minerals in rocks.

However, according to calculations, the decay of 1 km³ of granite rocks would release just a few dozen tons of lead from potash feldspar, while commercial lead deposits typically contain tens and hundreds of thousands of tons of this metal. After erosion of the platformal basement, layers of sedimentary rocks accumulate in adjacent basins. The lead enriches mainly clay layers. According to Lubchenko [19], the mean lead content in sandstones is $7 \times 10^{-4}\%$, in carbonate rocks $9 \times 10^{-4}\%$, and in clays $80 \times 10^{-4}\%$.

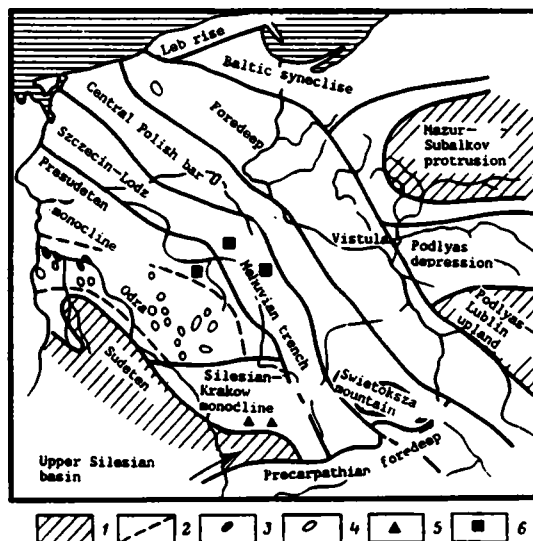


Fig. 2. Distribution of oil, gas, copper, and lead-zinc deposits in the Presudeten monocline (Poland): 1) protrusions of ancient rocks; 2) boundary between Permian and Triassic; 3-6) deposits (3-oil, 4-gas, 5-lead and zinc ore, 6-cupriferous sandstone and schist).

The sedimentary origin of these deposits and the theory of formation of commercial ores from metals washed down the continents by surface water [1, 7] in our opinion have not been properly substantiated. The following data contradict this view:

1. The absence of stratified textures in ores. For the most part, vein-inset, less often massive or striated, ores are found. Gustafson and Williams [8] rightly note that widespread vein ores are evidence of formations in sedimentary rocks that became hard to penetrate and fissured after premineralization diagenesis. The ore formation temperature and the composition of gas-liquid inclusions in metalliferous and vein minerals indicate [8, 26] that the ores were formed from buried hot brines.

2. Studies by Lubchenko [19] suggest that the age and pattern of salinity, the geochemical composition of water, the pH, and the hydrogen sulfide contamination did not affect the concentration of clark levels of lead in sediments of recent basins. This is due to the fact that lead is carried from eroded land to marine basins mainly as mechanical suspended matter with a negligible proportion of dissolved metal compounds.

As mentioned earlier, investigators often interpret metalliferous brines of various origin as the agent of mobilization, transport, and deposition of metals. These may be buried seawater and water of oil/gas basins or brines associated with evaporitic sediments. Circulation of metalliferous brines occurs through porous beds that function as conductors or in deep faults.

The association of stratiform lead-zinc deposits with the slopes of domes, rises, and crystalline massifs in our opinion is largely due to the fact that paleozones of the discharge of metalliferous brines were located near uplands, which played a key role in the formation of these deposits.

Deep faults are also known to have functioned as ore-conducting channels in which metalliferous brines circulated. Thus, a considerable number of lead-zinc deposits in sediments of platformal covers correlate closely with riftogenic structures formed, as mentioned in [28], along deep faults on subsiding tectonic blocks. In the Mississippi-Missouri area, an epigenetic commercial deposit is situated in riftogenic carbonate rocks. Numerous ore bodies are localized in near-rift carbonate breccias of wave-surf collapse and landslide origin. Metalliferous bodies of the Pine Point deposit in Canada are associated with a barrier reef stretching along a deep fault. The Tabornoe deposit and other lead-zinc ore shows in the Baikal polymetal belt are associated with bioherm and reef structures located in the deep fault zone. The Sardan deposits (Yakutia) are associated with bioherms and

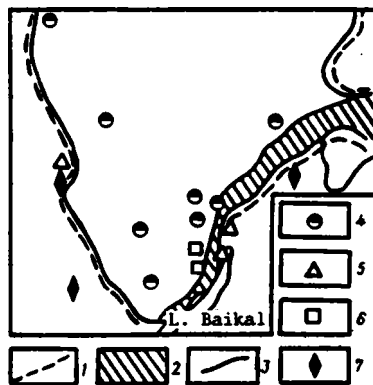


Fig. 3. Distribution of oil, gas, and ore deposits in the Lena-Tunguska oil/gas province: 1) boundaries of the Siberian Platform; 2) Baikal-Patom foredeep; 3) boundaries of the East Siberian oil/gas basin; 4-7) deposits and ore shows (4-oil and gas, 5-stratiform lead-zinc deposits, 6-gold-sulfide ores, 7-cupriferous sandstones).

biostromes of blue-green algae controlled by a deep fault zone bounding the Siberian Platform on the east.

The proportion of ore matter brought into the sea basin through washdown from land was insignificant, as indicated by the limited contribution of terrigenous material to the ore-enclosing deposits and by the heightened salinity and hydrogen sulfide contamination of local coastal-marine deposition basins, which rules out considerable freshwater influx.

The epigenetic nature of lead-zinc metallization in the Midcontinent zone of the United States relative to surrounding rocks is supported by the latest work by Maynard [20], which summarizes the results of many years of study of these deposits. He notes that the ores of Mississippi Valley deposits fill karst cavities in carbonate rocks, heightened porosity areas in bioherms, or fault zones. Mineralized solutions (more exactly, brines) contained 15% NaCl and had temperatures in the range of 90-160°C. In most deposits, vein minerals have a higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratio than the enclosing carbonate rocks, indicating an influx of some strontium into the system during dissolution of silicate minerals. The value of $\delta^{34}\text{S}$ in ore minerals varies from 0 to +10‰, which is higher than the respective estimate for sulfides in recent sediments and contradicts the hypothesis of a syngenetic origin of these ores.

Wodzicki [32] notes that the lead-zinc deposits of Upper Silesia were formed at metasomatic substitution of epigenetic dolomites. Sometimes, the ore fills cavities in karst breccias. In [10], lead-zinc ores of the Sardan deposit are described as formed after epigenetic dolomitization of carbonate rocks, suggesting similarities of ore formation processes in the Sardan ore province and in the Pine Point area. On the other hand, Maynard [20] notes that the first stage of lead-zinc metallization in Ireland (highly pyritic) took place early on during diagenesis of sediments, while lead and zinc sulfides were deposited at later stages in the development of the bed surrounding the ore.

LEAD-ZINC DEPOSITS AND CATAGENETIC PROCESSES

Determinations of postdiagenetic but premetamorphic stages in the alteration of rocks and sulfide mineralization disseminated in them was discussed in detail by Kholodov [26] and Kurilo et al. [17]. These studies are of special interest because they were conducted in Donbass bituminous coal deposits containing numerous coal seams of different grades, including bituminous, long-flame, gas, fat, coking, lean, baking, semianthracite, and anthracite varieties. The thermodynamic conditions of formation of coals of these grades in Donbass have been well studied and could serve as parameters in determining the formation conditions of their surrounding rocks. In analyzing the mineralogic and geochemical features of stadia

alterations of limestones in Donbass, Kurilo et al. [17] note that, during early catagenesis, which corresponds to long-flame and gas coal grades, the bulk of limestone is represented by fragments of organic remains, making up 70-90% of the rock volume and cemented by fine-grained slightly recrystallized carbonate. The subsequent change of the structure of the limestone involved intense recrystallization that reached a maximum at the boundary between the stages of cata- and metagenesis, which corresponds to formation of lean-baking/lean coals. According to these authors, the boundary between cata- and metagenesis in Donbass is documented at the transition from lean-baking (LB) to lean (L) in the temperature interval 170-180°C. In that interval, limestone is already fully recrystallized. It has no features of primary texture or structure, bioherms, or cement. The rock consists of medium-grained carbonate aggregations with microstylolitic and interpenetrating contacts formed during recrystallization in the course of dissolution and subsequent deposition of material as a result of high temperatures and pressures.

During metagenesis (lean, semianthracite, and anthracite), recrystallization involves a reduction in carbonate grain size. The resulting limestones consist of a dense material with no signs of preexisting organisms or cementing mass. The rocks are represented by aphanitic varieties (micrites) with a microgranular homogeneous structure. Authigenic mineral formation processes expressed mainly as dolomitization and quartzification are common in limestones. Quartzification begins to appear in limestones at the boundary between cata- and metagenesis, and it is associated with dissolution of terrigenous limestone material under temperature and pressure effects. Besides carbonate and quartz, bituminous materials contained in limestones are put into a migratory state. The variety of polycyclic aromatic hydrocarbon (PAH) with the highest bituminosity is observed in limestones of catagenesis zones, where bitumens are represented by heavy resinous fractions. In the lean-semianthracite interval a sharp drop in the amount of bituminous matter in rocks is observed, while there is a predominance of this matter among light oily compounds.

Another method of determination of stadiol epigenetic alterations in rocks of Donbass coal-bearing formations has been suggested by Kurilo [16]. This method is based on studies of the composition of authigenic minerals filling cracks and cavities, mostly conformal to the bedding of rocks of coal-bearing Middle Carboniferous strata in Donbass and characterized by linearity and an absence of any traces of near-vein alterations. He notes that calcite (CaCO_3 , 97-99.5%) is present in cracks that have experienced various epigenetic alterations. During medium catagenesis, calcite associates with barite, marcasite, and pyrite. This calcite typically includes oil-like materials and viscous bitumens in its gas-liquid inclusions. In late catagenesis conditions, marcasite disappears from minerals associating with calcite, while dickite appears. The degree of early metagenesis is clearly documented by the first occurrence of quartz, which is connected with the onset of dissolution of terrigenous material. As an additional method for determining the degree of diagenetic alteration, Kurilo [16] goes on to suggest the evolutionary series of sulfides, whose composition and characteristics vary in correlation with the intensity of these processes. In particular, sedimentary-diagenetic pyrite is observed in coaly-clay rocks near their contacts with coal and limestone layers as finely dispersed insets, small globules, pseudomorphoses after organic matter, and isolated crystals and aggregates in cubic octahedral and pentagonal dodecahedral forms. In the early and middle stages of catagenesis, corresponding to brown/long-flame, long-flame, and gas coal grades, pyrite-marcasite associations are common in these rocks, sometimes with melnikovite. It occurs in the cement of sandstones as irregularly shaped aggregations. In rocks of the catagenesis zone, pyrite is characterized by an excess of sulfur in its stoichiometric composition ($\text{FeS}_{2.10}$) and hole conductivity with a maximum thermo-EMF coefficient of +250 to +450 mV/deg. In the early stage of metagenesis, pyrite loses some of its sulfur and partly switches from hole to electron or mixed-type thermo-EMF. In late metagenesis, pyrite is converted to the electron variety, with an average stoichiometric composition $\text{FeS}_{1.88}$. This is accompanied by a decrease in the share of the heavy sulfur isotope from low degrees of postdiagenetic alterations to high degrees and a diminution of the Ni/Co ratio in the same direction. At the same time, pyrite grains become larger and develop a more perfect crystalline structure. A further temperature rise and splitting of sulfur produces a "pyrite-pyrrhotite" association. Pyrrhotite is associated with anthracite and is mainly represented by the hexagonal variety.

These data appear important, because in studies of lead-zinc deposits investigators often pay little attention to the degree of postdiagenetic alteration of rocks surrounding ore bodies or to the correlations between lead-zinc ore formation transformation processes and postdiagenetic development. It appears that, all other conditions being equal, higher temperatures and pressures are essential for formation of high lead and zinc concentrations and development of commercial ore deposits in locations in platform covers. High temperatures and pressures are conducive to redistribution of metals disseminated previously in rocks and creation of enriched areas and favorable structural and lithologic settings [12].

LEAD-ZINC DEPOSITS AND CARBONIC MATTER

The presence of carbonic matter appears to be an important condition for formation of lead-zinc deposits of this type. The average content of carbonic matter in the earth's crust according to various authors ranges from 0.02 to 0.07%. The subclarkes in various rocks are as follows (%): clay rocks 0.9, silty rocks 0.45, sandy rocks 0.20, carbonate rocks 0.20, salts and sulfates 0.10, coals 67.0, oil shales 16.5, and domanikites and bazhenites 6.

The content of carbonic matter in terrigenous and carbonate rocks where lead-zinc deposits of this type are situated typically varies from 0.5 to 4.5%.

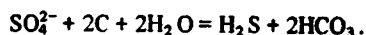
A characteristic feature of these deposits is their spatial association with oil/gas basins (OGBs). Lead-zinc deposits are often located in marginal parts of OGBs, in the so-called conservation zone, where oil decays and becomes converted to bitumens. This applies to the Upper Mississippi, southeastern Missouri, the Tri-State area, and other deposits in the United States (see Fig. 1), Upper Silesia in Poland (see Fig. 2), the Western Baikal region (see Fig. 3), Yakutia, and others.

Ore-enclosing deposits and sediments containing oil and bitumen accumulations have a similar geologic age and are thus linked not only spatially but also temporally. Their cooccurrence seems to also reflect the fact that both these lead-zinc deposits and oil/gas fields are located mainly on passive margins of paleocontinents, often in rift facies of carbonate rocks. Several authors who examined the Pine Point deposit and other western Canadian lead-zinc placers note, for example, that these deposits are situated in riftogenic structures that contain gas and bitumen signs. Apparently, hydrocarbons from the neighboring western Canadian oil/gas basin became concentrated in porous limestones of rift structures. Brines migrated from the center of the oil/gas basin, leaching metals from conductor beds, which were then deposited in carbonate rocks of basin margins [25].

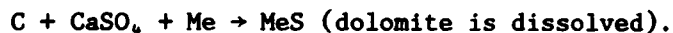
Evidence in favor of a paragenetic relationship between lead-zinc deposits of platform covers and oil/gas accumulations is also provided by the frequent finds in gas-liquid inclusions of ore and vein minerals that make up the lead-zinc ores, oils, and bitumens. Dolomite crystals in ores are often surrounded by a film made up of carbonaceous material. In the Buick deposit (southeastern Missouri), black sphalerites are enriched in hydrocarbons. An antraxolitelike material is often present as fragments among sulfides, and is cemented by them. Similar facts have been observed in many other lead-zinc deposits [31].

Investigators often note that the set of metals in gas-liquid inclusions containing Cu, Zn, Pb, Mn, Co, Ni, Ba, Ag, Cd, Sb, and F is similar to that in petroleum waters. The zinc content in petroleum ash is as high as 0.8%.

The factors responsible for the correlations between lead-zinc ores and carbonic matter may be diverse. One possible cause is the reducing property of carbonic matter, which, when reacting with sulfates, can form hydrogen sulfide according to this reaction:



Anderson [29], proceeding from equilibrium reaction calculations, showed that the interaction between organic carbon and calcium sulfate at 100-150°C in Mg^{2+} -containing brines lixiviates dolomites, provided that no metal cations are contained in the brine. If they are present, sulfides are formed and the dolomite is dissolved according to these schemes:



Another possible cause of this correlation is the role played by organic matter in bacterial life. Sulfate-reducing bacteria are heterotrophic and may exist at pH 4.2-10 and Eh from +110 to -500 mV at various temperatures. They prefer magnesium-rich solutions, and their abundance depends on the amount of decaying organics as an energy source. In a reducing environment in bottom sediments, sulfate-reducing bacteria are usually found in abundances of 10^3 - 10^5 per gram of sediment. Deposition of lead, zinc, and copper sulfides with participation of sulfate-reducing bacteria has been proved experimentally. Kramarenko [14] found galena, coveline, greenokite, and chalcopyrite. No sulfide formation was observed in tests without bacteria. The importance of sulfate-reducing bacteria in formation of lead and zinc sulfides is also supported by their presence in recent ore shows from the Gulf of Mexico [15] and the Bay of California [18].

The importance of organics in the formation of ore deposits also stems from the fact that organic material is conducive to development of metalloorganic compounds. Degens [9] demonstrated the presence of amino acids in stratal waters of oil-bearing provinces and carboxylic acids (up to 3 mg/liter) in deep and high-pressure waters of oil/gas deposits. According to Farfel' [24], alkaline waters of oil/gas deposits are characterized by heightened concentrations of hydrosulfide ions, which together with organic matter form strong complex compounds of metals and possibly ramified hydrosulfide-organic complexes. In an alkaline setting, bipolar compounds (such as amino and fulvic acids) have a complex-forming ability, and this is also true for humic and carboxylic acids, which form stable and well-soluble organic complexes with metals that can easily migrate in aqueous solutions (including complexes with Zn and Pb).

Various hypotheses have been advanced as to the origin of carbonic matter. Some postulate an organic genesis, associated with cata- and metagenesis of sedimentary rocks, while others suggest an inorganic origin, as a product received from the earth's mantle. With either theory, the close association of organic matter with lead-zinc stratiform deposits localized in platform covers is of obvious genetic and practical significance.

The role of oil/gas basins in the formation of lead-zinc deposits in carbonate rocks of platform covers in our view consists in the development in the peripheral zones of these basins of accumulations of bitumens in the course of discharge of rising oil/gas complexes. These bitumens subsequently facilitate (via biogenic or chemical mechanisms) formation of sulfidic sulfur and deposition of lead and zinc sulfides. On the other hand, the presence of oil/gas basins is also conducive to saturation with salts of groundwaters heated in cata-genetic conditions under the effect of evaporitic placers, typically present in oil/gas basin sediments, and conversion of these groundwaters to aggressive brines. As the brines migrate to marginal parts of the basin, they mobilize lead and zinc from rocks with heightened clarkes of these metals and carry them to bitumen accumulation areas, where the sulfides are then deposited.

LEAD-ZINC DEPOSITS AND EVAPORITES

The association of oil/gas shows with evaporites is well known. The association of evaporites with lead and zinc deposits localized in platform covers is less distinctly expressed. Such associations can be marked by the presence of sulfatic evaporites amid deposits making up the ore fields of lead-zinc metallizations, as illustrated by deposits in Canada (Pine Point), southeastern Missouri, Upper Silesia, Algeria, the Bogdo Bol'shoe ore show in the USSR, etc. However, evaporites are sometimes absent from the deposit itself and from ore shows, but are seen in adjacent areas in structural-formational blocks and zones from which metalliferous brines migrated into lead-zinc ore localization sites [7].

Popov [22] and Asanaliev [1] established that in many parts of Eurasia the carbonate rock strata that enclose lead-zinc deposits are under- and overlain by terrigenous or carbonate-terrigenous sediments containing gypsum and anhydrite layers.

Genetically, evaporites are probably conducive to various aspects of the formation of lead-zinc deposits. An important role is played by the interaction of groundwater with evaporites, resulting in a higher salinity and dissolving ability of aqueous solutions. Studies by Long and Angino [30] and Bogashova [3] found that, with rising groundwater salinity, the water becomes much more capable of leaching such metals as lead and zinc. These investigators also showed the possibility of lead and zinc transport in the form of haloid compounds.

Evaporites presumably play an important role as a source of sulfidic sulfur. With the participation of anaerobic bacteria, sulfate sulfur from evaporites is reduced to divalent sulfidic sulfur, which combines with metal ions to form sulfidic concentrations [4, 6].

Dolomitization of limestones is essential for development of stratiform lead-zinc deposits. It takes place in the postsedimentary stage and precedes precipitation of lead and zinc sulfides. The predominant view among ore deposit experts is that there are two genetically determined groups of dolomites: syngenetic (sedimentary) and epigenetic. However, recent studies have brought into doubt the common occurrence of syngenetic dolomites in the Phanerozoic. Careful studies of recent carbonate accumulation in oceans have indicated that recent carbonate sediments are almost totally calcareous. As to geosynclinal sediments, there is a dramatic rise in calcium and magnesium concentrations in carbonate rocks from the Late Precambrian through the Mesozoic, as noted in [23]. Generally, marine dolomite formation displays two trends: attenuation with geologic time and a decrease from shallow-water to deep-sea regions.

In [13] it was noted that dolomite formation from oversaturated low-temperature groundwaters is an extremely slow process that is practically unreproducible. The rate of dissolution and crystallization of calcite is 100 times as high as that for dolomite, and calcite is predominantly deposited in such conditions. The dolomite formation process evolves through a sequence of stages: magnesium-containing calcite - protodolomite - dolomite [13]. The bulk of postsedimentary dolomite is a result of limestone substitution. The possibility of substitution of carbonate rock calcium by magnesium from brines follows from the energetic efficiency of the dolomitization process, from experimental studies, and from the geochemistry of primary sedimentary brines, which in the course of evaporative evolution requires high magnesium concentrations. However, certain natural factors sharply accelerate dolomite formation processes [13]. In particular, with a rise in the NaCl concentration in solution to 4 M, the dolomitization rate is tripled. In a natural environment, increased temperatures is presumably a leading factor.

Experimental synthesis of dolomite has succeeded only at relatively high temperatures: at 150°C small amounts of dolomite were obtained, while at 200°C the solid phase consisted mainly of dolomite. Observations of recent dolomitization suggest that it occurs between 250 and 295°C. A temperature increase of 10°C accelerates the dolomite-for-calcite substitution reaction by a factor of 2.2. In the Paleozoic of Pripyat Valley, the paleotemperatures of dolomitization of carbonate rocks ranged from 150 to 240°C. However, a necessary condition of dolomitization is a high magnesium concentration in brines (a high Mg/Ca ratio). The optimum magnesium concentration is 50 g/liter [13].

Dolomitization processes result in accumulation of Ca, Sr, Pb, and Zn in sedimentary brines. Zinc content in the high-calcium most metamorphosed brines reaches $n \times 100$ mg/liter, while for lead this figure is $n \times 10$ mg/liter. According to calculations by Roedder [31], a minimum of 1 g of metal must be deposited from each ton of brine for a lead-zinc deposit to be formed over 10^5 years at geologically possible fluid flow velocities. A brine can be metal-forming if it contains at least 1-10 g/ton of the respective element. The above-cited lead and zinc concentrations in brines, as noted in [13], correspond to contents of these elements observed in gas and liquid inclusions of minerals in stratiform deposits.

According to the data cited in [17], dolomitization of limestones in Donbass Carboniferous sediments began in the initial stages of catagenesis (or perhaps even during diagenesis). In this case, dolomite as rhombohedral crystals replaces selectively fine-grained calcite of cement, while coarse-grained calcite remains unaltered. The quantity of such dolomite crystals in limestones during the stage of catagenesis does not usually exceed 5%; during metagenesis the dolomitization is more widespread (up to formation of dolomitic limestones).

The proportions of epigenetic dolomites and lead-zinc metallization suggest a close interrelationship, although metallization is superimposed upon dolomitization. As an example of such interrelations, one can cite observations by Bagno and Mashir [2] conducted on ore shows in the Carboniferous of the southern slope of the Voronezh anticline and confirmed by other geologists. Dolomitization and metallization were found to be localized within the Namurian stage. Ore mineralization is somewhat shifted up the section relative to dolomites. In plan, the metallization area coincides with the dolomite field. The maximum metal concentrations and the thickness of mineralized rocks are observed on the same areas where the

maximum thickness of dolomite rocks was documented. In plan, these areas tend to coincide with fault zones. Outside the dolomite field, where the Namurian rocks are represented by limestones, no ore mineralization is found. Ore and dolomite mineralization exhibit a clear metasomatic nature and are superimposed on the surrounding limestones.

The presence of faults, including regional ones, is a typical feature of stratiform and other types of lead-zinc ore deposits. The faults serve as channels for migration of metal-liferous brines within ore fields and often are seen to link lead-zinc deposits with adjacent oil/gas basins and evaporite placers. An abundance of faults is conducive to integrated migration of brines, which flow around large rock blocks, with intensification of the dissolution of metals contained in the rocks of these blocks.

Long-lived faults also function as ore-conducting channels when metalliferous brines are discharged through them.

Thus, lead-zinc ore deposits localized in platformal cover rocks are formed under combinations of favorable conditions, including the following: 1) areas of marine basins with deposition of limestones (often reef limestones) and less often dolomites located on slopes of shields and midoceanic massifs, and often on passive continental margins; 2) spatial proximity of oil/gas basins and the presence of bitumens and other hydrocarbons in the ore-bearing carbonate formation; 3) spatial proximity to evaporite placers with predominance of gypsums and anhydrites; 4) presence of regional faults cutting across oil/gas basins, evaporite placers, and development areas of ore-bearing formation; 5) widespread siltstone-argillite sediments that have passed through meta- and catagenesis; and 6) widespread evaporitic dolomites.

All these conditions can be regarded as predictive exploration criteria to be used in assessing the prospects for the covers of the East European and Siberian platforms and in planning purposive regional exploration for lead and zinc deposits.

The East European Platform is known to be largely similar in geologic structure to the North American Platform, where the sedimentary cover contains a large number of important lead and zinc ore deposits. Besides similarities, the developmental history of these structures reveals important differences. Particularly notable is the intense formation of salt-bearing strata in the North American Platform during the Silurian, Devonian, and Carboniferous in the Michigan, Yellowstone, and other basins. In the meantime, most of the East European Platform experienced only local dolomite and sulfate formation, except for the Pechora anticline, where salt-bearing beds were laid down. In this context, the Pechora structure may be a promising object for lead and zinc ore exploration.

The Siberian Platform is more similar to the North American platform in terms of evaporite occurrence. From this point of view, the prospects for discovering stratiform lead-zinc deposits are more significant in this region. However, further study is needed to obtain more accurate estimates of the commercial potential of stratiform lead-zinc metallization in the East European and Siberian platforms.

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GEOCHEMICAL AND GEOTECHNOLOGICAL ACCESSORY CHEMICAL ELEMENTS IN STRATAL INFILTRATIONAL URANIUM DEPOSITS

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UDC 550.4/553.495

Variable-valence chemical elements susceptible to oxidative lixiviation from rocks are classified as geochemically accompanying elements in infiltrational-stratal type uranium deposits (Se, Re, Mo, and V). Like uranium, they form insoluble clay matter in the low-valence state. Geotechnologically accessory elements are chemical elements with constant valence, which are brought by selective sulfuric acid lixiviation in industrial solutions to concentrations sufficient for commercial exploitation (Sc, Y, lanthanoids, and other rare and trace elements that form strong sulfate complexes).

A number of accompanying chemical elements have been found in stratal-infiltrational uranium deposits both of subrecent and ancient type. Some of these elements can be brought into commercial mining by underground lixiviation.

A genetic correlation of accumulation with uranium in reducing geochemical barriers has been established for selenium, molybdenum, and rhenium. These elements form overlapping or consecutive zones of epigenetic concentrations in areas with a lowering of the groundwater redox potential from positive to negative values [10-12, 18].

In recent years, accumulation of scandium, yttrium, lanthanoids, and other rare and dispersed chemical elements has been reported in such uranium deposits [14, 18, 19]. Their association with uranium has been attributed to the spatial coincidence on the terminal portions of stratal oxidation zones of reducing and neutralizational chemical barriers. The latter are believed to be formed as a result of rocks neutralizing the oxidation products of iron disulfides contained in metalliferous horizons [19].

This attractive theory of coincident precipitation sites of anionogenic elements of variable valence and elements of hydrolyzates that retain a constant valence in natural conditions must be rigorously matched against the actual hydrogeochemical data for terminal portions of stratal oxidation zones. We will discuss the available information relevant to this theory.

According to published data [9, 11, 20], the pH value of waters in oxidizing (incompletely oxidized) rocks in the terminal portion of stratal oxidation zones sometimes drop to 6.3 but more often to 6.6-6.7, as against 7.6-8.0, and rarely more, in oxygen waters in adjacent fully oxidized rocks. Such pH lows have also been established in zones of intense biochemical oxidation of bitumens in carbonate rocks with complete absence of signs of oxidation and accumulation of hydrogen sulfide and carbon dioxide in the solution [17, 20]. These data have been obtained by the present authors in tests of groundwater spontaneously effusing from wells and boreholes and sources in quarries and mines. They have been interpreted as representing nonequilibrium hydrogeochemical conditions formed in zones of intense accumulation of oxidation products during the course of biochemical and redox interactions [11, 17].

Figure 1 provides three illustrations of a detailed analysis of pH value distributions on terminal portions of stratal oxidation zones in different lithologic terrigenous complexes. They include zones of stratal oxidation developed in Upper Cretaceous arkosic alluvial sands, in Upper Cretaceous polymictic sands with glauconite of littoral-marine type, and in Paleogene oligomictic well-softed quartzose sand in a marine shoal setting. The measurements of pH values in waters from hydrogeologic boreholes in interstitial solutions extracted from cores immediately after lifting to the surface, and in waterlogged pastes, also vacuumized

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TABLE 1. pH Values of Water in Principal Geochemical Types of Rocks of Metalliferous Horizons of Stratal Infiltrational Deposits

Geochemical rock type	Sampling object	Number of samples	Average $\bar{x}$	Standard deviation σ_{n-1}	Biased standard deviation σ_n	$x_{\min}$	$x_{\max}$
Brown-yellow rocks from stratal oxidation zones	Self-effusing hydrogeologic boreholes	59	7.4	0.21	0.21	7.0	8.0
	Interstitial solution in core from borehole	29	7.6	0.21	0.21	7.1	8.0
	Water-saturated paste from borehole core	81	7.3	1.14	1.13	6.9	8.1
Yellow-gray and gray-yellow rock from incomplete stratal oxidation zones	Self-effusing hydrogeologic boreholes	29	7.4	0.30	0.29	6.9	8.1
	Spring in a mine	19	6.9	0.53	0.52	6.3	8.1
	Interstitial solution in core from borehole	14	7.5	0.41	0.40	7.0	8.5
	Water-saturated paste from specimen (including ore)	52 (8)	6.0 (5.2)	1.8 (0.71)	1.7 (0.67)	1.0 (4.5)	8.1 (6.3)
Gray unoxidized rock	Self-effusing hydrogeologic boreholes	98	7.5	0.25	0.25	7.0	8.3
	Interstitial solution from borehole core (including ore)	109 (7)	7.7 (7.6)	0.29 (0.28)	0.29 (0.26)	6.9 (7.2)	8.5 (8.1)
	Water-saturated paste from core (including ore)	757 (26)	7.5 (7.2)	0.26 (0.25)	0.26 (0.25)	6.4 (6.9)	8.5 (7.7)

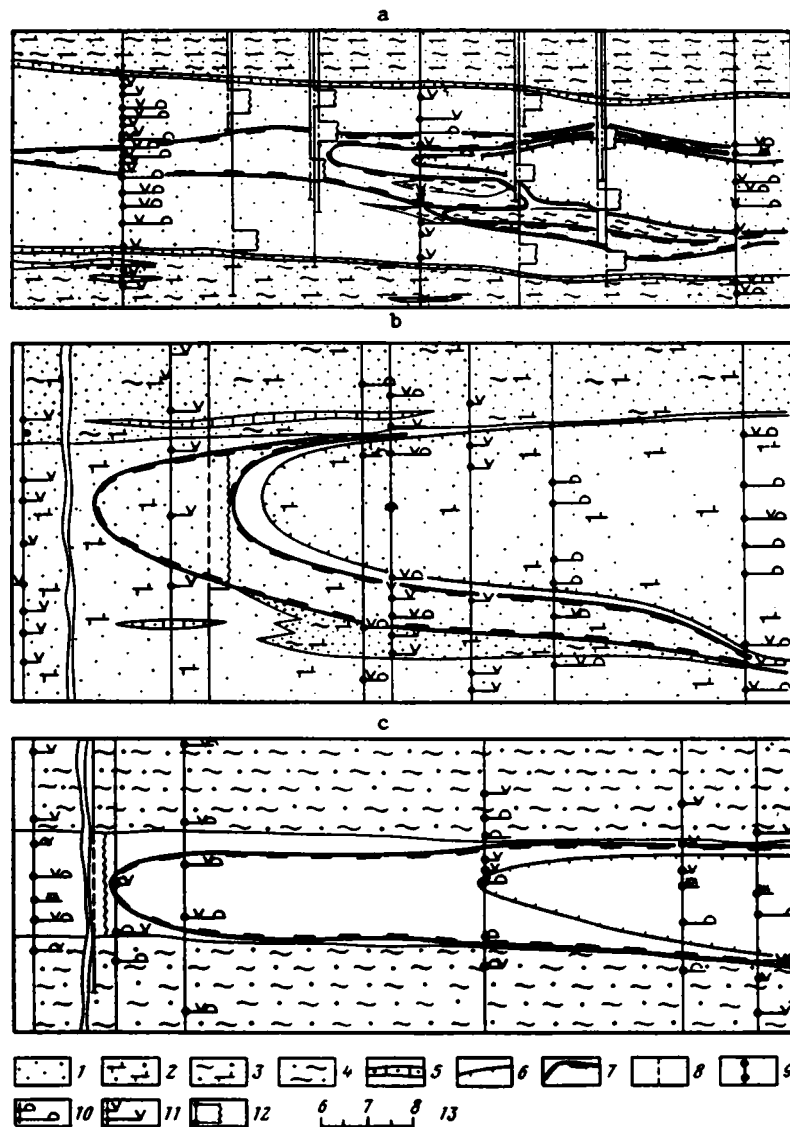


Fig. 1. Values of pH of aqueous solutions at the terminal portions of stratal oxidation zones: a) in arkosic alluvial Upper Cretaceous sand; b) in poly-mictic Upper Cretaceous littoral-marine sand with glauconite; c) in oligomictic quartzose Paleogene sand of marine shoal; 1-4) sand [1) fine-grained, 2) slightly carbonaceous, 3) fine-grained carbonate sandstone interlayer, 4) with a roiling texture]; 6-7) contours [6) stratal oxidation zone, 7) ore body]; 8) filtration interval of the hydrogeological well; 9) core sampling site; 10-12) pH values [10) interstitial solution from a core specimen, 11) tightly sealed water-saturated paste of a specimen, 12) water from hydrogeological borehole]; 13) scale of numeric pH values (pH = 7 on borehole axis).

immediately after the cores were lifted to the surface show no clear correlation between the position of the specimen and the boundary of the stratal oxidation zone.

Table 1 presents the results of statistical processing of all reliable data available to us on pH values of aqueous solutions in rocks of metalliferous horizons of subrecent stratal infiltrational deposits. Statistical groups of water samples are combined separately for the three main geochemical rock types: gray unoxidized, brown-yellow stratially oxidized, and intermediate yellow-gray incompletely oxidized. Within the geochemical types, the statistical groups are subdivided according to the geological objects or testing methods. Data on the pH of aqueous solutions from spontaneously effusing hydrogeological wells, those isolated from cores of drilling column holes, and those measured in waterlogged vacuumized

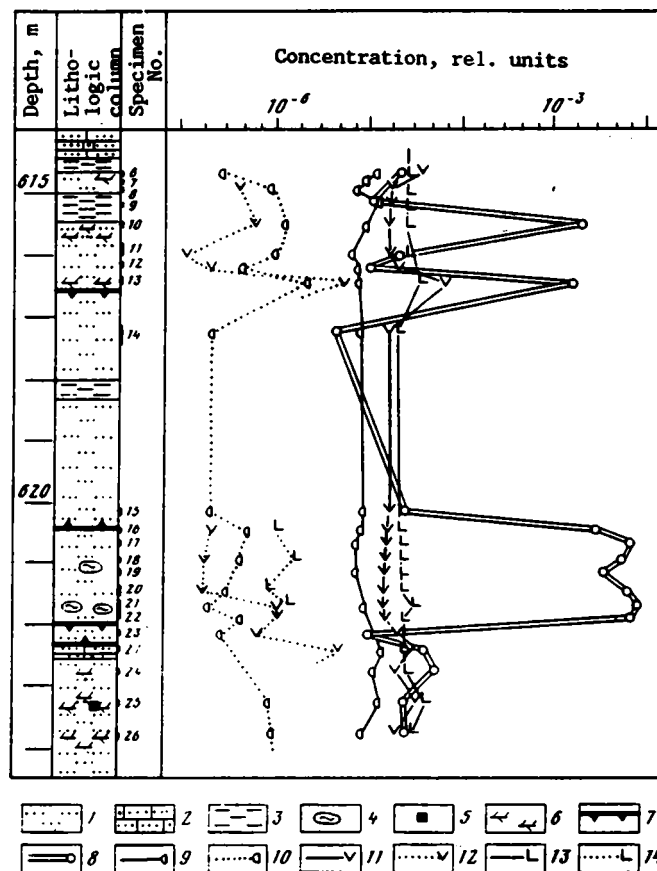


Fig. 2. Distribution of uranium, scandium, yttrium, and lanthanum in a section of a metalliferous horizon: 1) fine-grained sand; 2) carbonate sand; 3) siltstone; 4) clay pellets; 5) iron disulfide isolation; 6) carbonified plant remains; 7) boundary of stratal oxidation zone; 8) uranium concentration in rock; 9, 10) scandium concentration [9) gross, 10) acid-soluble]; 11, 12) yttrium concentration [11) gross, 12) acid-soluble]; 13, 14) lanthanum concentration [13) gross, 14) acid-soluble]. Uranium in rocks and sulfuric acid extracts determined colorimetrically with arsenazo III) (analyst L. S. Shulik). Scandium, yttrium, cerium, and lanthanum determined by quantitative spectral method [analysts A. I. Galuzdina (rocks), G. E. Belousov, (solutions)].

pastures from core specimens are analyzed separately. The pH values from testing of water sources in mines, i.e., in conditions with an artificial intensification of water exchange and rock oxidation, were treated separately.

The data from testing of formational waters flowing out spontaneously from hydrogeological boreholes are descriptive of the composition and properties of solutions averaged for the entire volume of water-releasing rocks within the range of the hydraulic effect of these wells. These rock volumes amount to tens of hundreds of cubic meters and usually encompass more than one lithological type. Testing data for these wells found no significant differences between the pH values of water within geochemical types. At an average pH of 7.5, fluctuations of 0.5 are observed in any of the lithogeochemical zones, so that no general pattern of pH variation caused by replacement of oxidative settings by reducing settings can be established.

The interstitial solutions from cores characterize a rock volume of tens of cubic centimeters and correlate directly with point testing in lithologic and geochemical exploration. According to the average pH values, interstitial solutions from the rocks of these geochemical types are almost identical.

The mean pH values for interstitial solutions extracted from cores immediately after they were lifted to the surface was around 7.6 ± 0.1 , with variations from 6.9 to 8.0-8.5, which are practically equal in all lithogeochemical types.

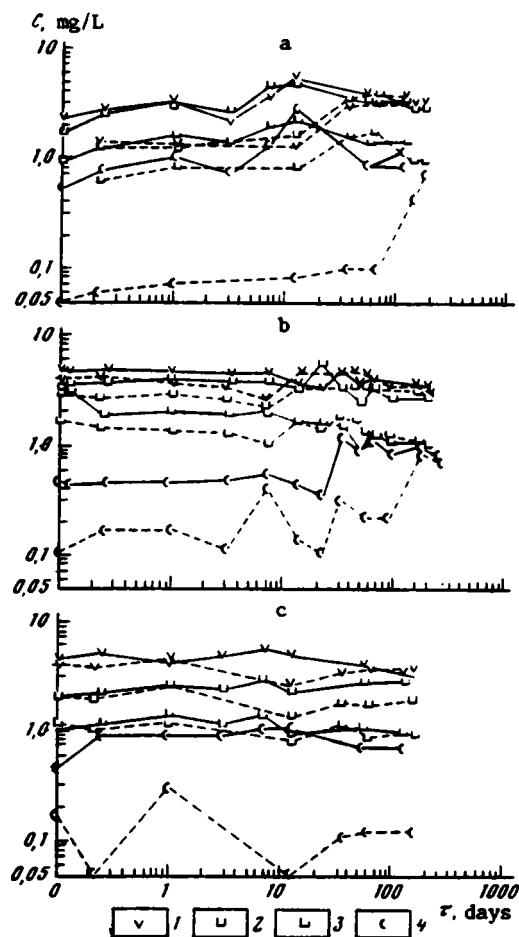


Fig. 3. Concentration of Y, Ce, La, and Sc in sulfuric acid solutions vs. time of lixiviation from clay-slit fraction of terrigenous rocks: a) specimen 054, brown-yellow stratially oxidized rock (C_{org} 0.01%, CO_2 0.2%, Y 45 g/ton, La 36 g/ton, Sc 36 g/ton); b) specimen 060, light-gray unoxidized rock (C_{org} 0.02%, CO_2 1.35%, Y 42 g/ton, La 35 g/ton, Sc 33 g/ton); c) specimen 059, dark-gray unoxidized rock (C_{org} 0.25%, CO_2 3.72%, Y 50 g/ton, La 41 g/tin, Sc 26 g/ton); 1-4) variation of yttrium, cerium, lanthanum, and scandium concentrations, respectively, at pH 1 (solid) and pH 2 (dashed).

The generally higher pH values (by 0.1-0.3) of interstitial solutions compared to self-effusing waters apparently reflect a loss of gaseous oxygen components, such as CO_2 , during partial degassing of the solutions as they were released and flowed into the sampler. The ore specimens are indistinguishable from surrounding rocks in terms of the pH values of their interstitial solutions.

We see that both in a macrovolume of several cubic meters and on a narrowly local scale in a volume measured by tens of cubic centimeters the transfer of water solutions from oxidized to reduced rocks at the terminal portion of stratal oxidation zones is accompanied by an insignificant change in the pH. This change is much smaller than the pH variations within geochemical types. The redistribution of chemical elements associated with pH variations within the subneutral and slightly alkaline media may occur both at the terminal portions of the stratal oxidation zone and equally within the geochemical zones, including the contacts of minerals and rocks responsible for substantially different pH values.

Signs of greater pH variations are observed in conditions of artificial oxidation of rocks and minerals. As is well known, after prolonged storage of monolithic cores in air, specimens enriched in sulfides exhibit an abnormally high acidity, resulting from oxidation of the sulfide material. Pyrite specimens in such conditions acidulate an aqueous solution to a pH ~1, while unoxidized specimens produce a pH ~7 [11].

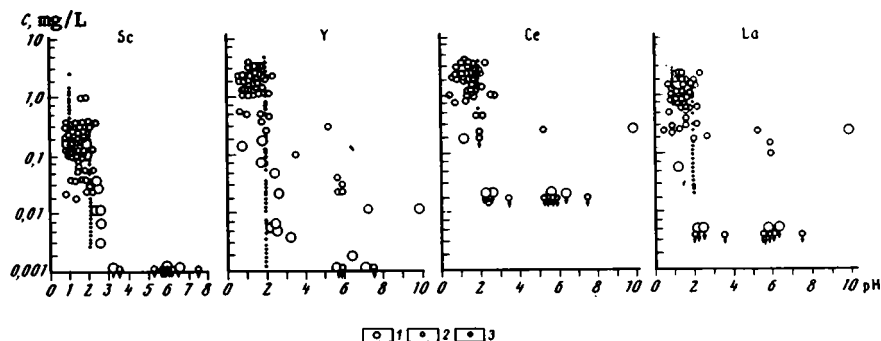


Fig. 4. Scandium, yttrium, cerium, and lanthanum concentrations vs. solution pH: 1) groundwaters (literary data with supplments); 2) technological solutions in areas of sulfuric acid underground lixivation of uranium, stratal infiltrational deposits; 3) sulfuric acid extracts from terrigenous rocks of metalliferous horizons of stratal infiltrational uranium deposits. Analysis of technological solutions and sulfuric acid extracts performed at the Spectral Laboratory of the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Academy of Sciences of the USSR (analyst G. E. Belousov).

The generally heightened acidity of water sources from incompletely oxidized rocks in quarries and mines with an average pH up to 6.9, varying from 6.3 to 8.1, is also probably associated with an artificial intensification of oxidation and a change in regime due to a lowering of the groundwater table after water extraction.

Redox and acid-alkaline equilibrium between an aqueous solution and rocks and minerals in conditions with complete utilization of dissolved oxygen as on the terminal portions of stratal oxidation zones are modeled in first approximation by Eh and pH values in tightly sealed water-saturated pastes [9, 10]. Based on hundreds of measurements, fresh rock specimens from metalliferous horizons of stratal infiltrational uranium deposits that have not been oxidized in air yield pH values from 6.4 to 8.5. The average pH from measurments on 757 gray rock specimens from different locations and deposits is 7.5. In this group, 25 ore specimens have pH values from 6.9 to 7.7 (average 7.2), which is indicative of some acidulation of the medium in the metallization zone.

Ore specimens from the collection (i.e., after long storage in air) exhibit a much higher acidity. On average, for 8 such specimens the average pH was 5.2, varying from 4.5 to 6.4. Pyritized rocks enriched in carbonic matter when stored in air can result in even higher acidity (up to 1). The average for 52 specimens of incompletely oxidized rocks stored in the collection was 6.1, and the maximum in sulfide-free rocks was 8.1. This means that an acid medium is created in oxidizing rocks only with free oxygen access. The terminal portions of stratal oxidation zones receive dissolved oxygen in trace amounts measured by small fractions of a milligram per liter. Given that formation waters migrate at rates of a few meters per year, one should not be surprised that there is not substantial acidulation at the medium at the stratal oxidation front.

Fully oxidized rocks of metalliferous horizons produce an average pH of 7.3, with variation from 6.9 to 8.6. Compared to the initial gray rocks, yellow limonitized rocks generally have pH values lower by 0.2, presumably reflecting the effects of hydrolytic acidulation typical for oxidation of ferrous iron.

The differences in acidity associated with local segregations of pure oxidized mineral and organic substances contained in rocks of metalliferous horizons [10] and the above data of pH measurements suggest the possibility of local acid-alkaline nonequilibrium in incompletely oxidized rocks and at the boundary of heterogeneous substances within geochemical zones. This microzonal acid-alkaline differentiation may produce local transformation and redistribution of matter, but apparently without any substantial import or export. Microzonal acid-alkaline redistribution of chemical elements on the terminal portions of the stratal oxidation zone can only attain magnitudes associated with 0.1-0.2 pH value variations. In artificial conditions of activation of oxidation by the passage of rock tunnels, this range may be increased to 1, and to several units in aerated specimens.

In an analysis of the scale of acid-alkaline redistribution of individual chemical elements associated with redox interactions at the terminal portions of stratal oxidation zones with inclusion of the above data, one should be cautious in making predictions as to possible accumulation in these locations of elements that do not change their valent state in the natural redox potential range. In proposing interpretations of uranium association with chemical elements with an entirely different geochemical behavior, one should be mindful of possible artifacts because of disregard for other factors of redistribution, i.e., without the presence of the so-called minimum of the system studied.

The genetic characteristics of rare and scattered chemical elements in enclosing rocks of infiltrational stratal uranium deposits can be at least of three types: epigenetic, diagenetic, and sedimentary. This can be illustrated by scandium, which is a typical representative of a disseminated chemical element. It is classified as a rare element not only because of its paucity but also because of the fact that it does not form separate commercial deposits. A clarke of scandium in sedimentary rocks according to Vinogradov [5] is 10 g/ton. According to Beus [2], a clarke of scandium in clayey schists is 13 g/ton, and in sandstones in carbonate rocks just 1 g/ton. According to recent data [7], a clarke of scandium in the earth's crust is 16.6 g/ton. In sedimentary rocks, the mean scandium contents are distributed as follows (g/ton): clays 11.3, deep-sea clay 23.2, limestone 1, sandstone 6.8. Sandstone varieties enriched in ilmenite, rutile, monazite, and zircon are also the richest in scandium. Mature sandy rocks with a sharp dominance of quartz are depleted of scandium (up to 1-2 g/ton).

Scandium concentrates in basic rocks, and higher scandium concentrations are observed in sedimentary rocks and crusts of weathering - in connection with its source in basic rocks. Borisenko [3] distinguishes the following principal scandium deposits. He cites the following weight concentrations (%): ferrimuscovite 0.4, wolframite 0.25, cassiterite 0.13, beryl 0.13, zircon 0.12, mica 0.05, monazite 0.03, ilmenite 0.02, and fluorapatite 0.02.

In the deposits discussed herein, uranium sands are enriched in scandium up to 5 g/ton as against 2-4 g/ton in initial gray sands [19]. Syngenetic scandium concentrations in clays at these deposits are at the level of 10-15 g/ton. Besides exogenous epigenetic concentrations, scandium may have been brought with an equal probability into the sands with clastic minerals, including placer accumulations. It may have also formed diagenetic accumulations in phosphate residues and in clay cement. The actual proportions of the magnitude of subclarke epigenetic redistribution and the proportion of scandium concentrations in allo- and authigenic minerals containing scandium and the amount of scandium sorbed by clay cement may only be determined by a detailed analysis. Otherwise, the classification of the scandium in uranium-bearing rocks as epigenetic is dubious.

Scandium accumulation in uranium-bearing sands as a result of its acid-alkaline redistribution has been linked to hydrolysis, which is known to start for scandium salts at a pH of 4.8-4.9, reaching a maximum at 8.5. Shmariovich et al. [19] have conducted experiments which indicated that the minimum of scandium oxide solubility is at pH 9.5-10 (10^{-7} g/liter). In subneutral and weakly alkaline stratal waters of these deposits, scandium concentrations should not exceed 10^{-6} g/liter and more likely is 10^{-7} - 10^{-8} g/liter according to their calculations [19]. This shows a poor correlation between the physicochemical data and the assertion by these investigators of a significant redistribution of scandium in the profile of ore-controlling zonality of stratal infiltrational uranium deposits. Their experimental data on the pH drop to 4-3 as a result of sulfide oxidation under free air oxygen access, though applicable to formation of acid waters of sulfide deposits aerated in oxidation zones [11], are not realized in the terminal portions of stratal oxidation zones.

Underground sulfuric acid lixiviation of uranium ores in stratal infiltrational deposits is always accompanied by an influx of scandium concentrations of fractions of milligram per liter into the productive solutions. In deposits adjacent to discharge areas of clastics from territories with widespread presence of basic rocks, the concentration is as high as a milligram per liter. In solutions pumped out from area of oxygen-carbonate lixiviation, practically no scandium is found, which is contrary to the suggestions [19] of underground lixiviation of scandium according to sulfuric acid or bicarbonate processes.

As typical representatives of rare-earth elements, scandium, as well as yttrium and lanthanum, are found in productive solutions from sites of sulfuric acid underground lixiviation also when their concentrations in the rocks are close to clarke. As an illustration

of this possibility, Fig. 2 presents the geochemical section of a borehole that penetrated to uranium ore intervals of aquiclude horizons. The figure clearly shows how the uranium metallization is controlled by the upper and lower boundaries of stratal limonitization zones. Along these zones, metallization is localized in unoxidized rocks. Scandium, yttrium, and lanthanum contents display no unambiguous correlation with the uranium distribution. A slight correlation with the argillicity of rocks is observed for scandium. Yttrium tends to be associated with rocks enriched in vegetable remains. Lanthanum is distributed more monotonically, although it replicates the yttrium distribution curve in a smoother pattern.

The distribution of these chemical elements in the acid-soluble part of rocks is more variable. Unlike uranium, which is completely leached from rocks by sulfuric acid with potassium permanganate, scandium, yttrium, and lanthanum are lixiviated to a lesser degree in such conditions. The contents of their acid-soluble component are lower by an order of magnitude than their gross content in the rocks. Replicating in a more contrastive form the distribution curves of their gross content, oxygen-soluble forms near the redox boundary for iron display an upsurge in acid-soluble forms of scandium and especially yttrium. The behavior of lanthanum is ambiguous. These surges in the concentration of acid-soluble scandium and yttrium forms may be related to the microzonal acid-alkaline inhomogeneity discussed earlier and the possible alteration of the forms of disseminated elements, so that their forms in the rocks become less stable.

During the course of weathering and transport of weathering products, the clay fraction becomes enriched in rare-earth elements (REEs). The silt fraction largely retains its initial composition. The sand fraction becomes on the whole depleted, although mechanical differentiation may enrich some interlayers and areas because of accumulation of stable minerals [21, 22]. Both relict minerals and finely dispersed true hypergenetic minerals (REE carriers) also accumulate among weathering products [4, 15, 16]. Epigenetic neomorphs should also accumulate in the finely dispersed fraction. For this reason, in experiments with sulfuric acid REE lixiviation from rocks of metalliferous horizons of the stratal infiltration uranium deposits, we took the clay-silt fraction of terrigenous rocks. This fraction was accumulated separately for the three representative geochemical rock types: yellow, light-gray, and dark-gray.

Kinetic experiments were performed according to the Morse method [23] in H_2SO_4 solutions with pH 1 and 2 of steady acidity, as is normal for sulfuric acid underground uranium lixiviation. To maintain the solid-to-liquid phase ratio of 1:2, the lixiviation process was interrupted for different time periods. In both series of experiments (pH 1 and 2), the specimen was divided into 10-15 parts, 50 g each, which were lixiviated for different lengths of time. To maintain the pH at a constant level, the solution was periodically strengthened with a 10 N H_2SO_4 . The pH values were monitored electrometrically with a glass electrode and measured on an OP-211 potentiometer.

The kinetic experiments also indicated that acid-soluble forms accounted for just 10-20% of the gross concentration of rare-earth elements in rocks. The bulk of this acid-soluble phase is leached out during the first day, i.e., represents mostly the lightly soluble form (Fig. 3). Scandium is the most difficult to lixivate, especially at pH 2. At pH 1 it passes into solution with a delay compared to other elements of this family. The effect of the geochemical rock type is expressed in less intense lixiviation of brown-yellow rocks than in light- and dark-gray varieties. The specifics of the hypergenetic lixiviation of these elements in the course of transformation of initial rocks to stratally oxidized rocks may be responsible for the difference.

The possibility of sulfuric acid lixiviation of scandium, yttrium, and lanthanoids from rocks with subclarke contents of these elements is also confirmed by the data on natural acid solutions. Such solutions are common in recent volcanic areas.

According to Miklishanskii et al. [13], scandium and cerium concentrations in the acid waters (pH 1.25) at the source of the Yuryeva River (flowing from Ébeko volcano on Paramushir Island in the Kuriles) are 0.13 and 0.19 mg/liter, respectively. Concentrations of hundreds of milligrams per liter of Ga, La, Pr, Sm, Dy, Er, and Yb have been detected in this water. According to Baskov and Surkov [1], the acid waters from Ébeko volcano (pH 0.8) contain 0.15-0.37 mg/kg of scandium and 0.15 mg/kg of yttrium. Scandium and yttrium concentrations in the Nizhnemendelev source on the slope of Mendelev volcano (Kunashir Island) at pH of

1.75 are 0.16 mg/kg each. Scandium is found in acid waters, but is absent from subneutral and slightly alkaline waters.

The enrichment of acid waters in the springs and volcanic regions in scandium, yttrium, and lanthanoids is close to the levels observed in productive solutions of underground sulfuric acid lixiviation of ores in infiltrational uranium deposits. The slightly lower concentration in springs may be due to the fact that in crack collectors of volcanic structures solutions are farther from equilibrium with the rocks than they are in porous sands of metalliferous horizons at underground lixiviation sites.

Scandium is practically insoluble in subneutral and alkaline groundwaters. In subneutral stratal waters of metalliferous horizons, scandium contents according to instrumental neutron activation analysis (NAA) is at the levels of tens of micrograms per liter. In seawater its mean content is 0.0008, in groundwater of the hypergenesis zone an average of ~ 0.1 , and in hot springs 0.003-0.02 $\mu\text{g/liter}$ [7]. Unlike scandium, the other two minerals — yttrium and lanthanum — lixivate intensely also in an alkaline hydrogeochemical environment. According to Krainov [8], waters with pH 9-10 in agpaitic syenites contain tens of micrograms of yttrium per liter and hundreds of micrograms of cerium and lanthanum. On the other hand, less alkaline waters (such as nitrogen hot springs) are devoid of analytically detectable concentrations of these elements. In stratal waters in the areas of these uranium deposits, lanthanum and cerium contents according to NAA are within fractions of a microgram per liter.

Figure 4 plots scandium, yttrium, cerium, and lanthanum contents vs. pH values of lixiviating solutions and groundwaters. The curves show that, in groundwaters, sulfuric acid solutions in underground lixiviation sites, and sulfuric acid extracts from rock specimens there does not appear to be any analytically detectable scandium concentrations ($>1 \mu\text{g/liter}$) before pH <3 . A further rise in the acidity is accompanied by a higher scandium concentration, which increases to fractions of a milligram and even several milligrams per liter. Yttrium, cerium, and lanthanum in such strongly acid media also pass into the solution. In technological solutions and in sulfuric acid extracts they reach higher concentrations than does scandium. Their normal concentrations in such solutions attain several milligrams per liter.

Since subclarke concentrations of a substance are always lower than the contents of the main metalliferous components by one or more orders of magnitude, one can expect production of commercially profitable amounts of accessory materials extracted from essentially permeable rocks only if production is conducted on a large scale.

At usual contents of these accessory components in technological solutions of underground lixiviation areas of 0.1-10 g/m^3 and an average productivity of pumping wells of 100-300 m^3/day , an annual output can range from 3.6 to 1096 kg from a well. These estimates suggest that extraction of rare and disseminated elements as a byproduct of lixiviation solutions can be profitable and be sufficient to meet the industrial demand for these materials.

In stratal infiltrational uranium deposits and in other deposit types, one can distinguish two groups of chemical elements accompanying the main metallization: 1) geochemical accompanying elements, including chemical elements that constitute concentrations formed by a common metallization process (in stratal infiltrational uranium deposits, these include selenium, molybdenum, rhenium, and possibly vanadium, i.e., elements with variable valence subject to oxidative lixiviation and forming insoluble compounds in a low-valence state); 2) geotechnological accompanying elements, which include elements lixiviated selectively from rocks whose concentrations in the pumped-out solutions rise to levels necessary for profitable extraction. In sulfuric acid lixiviation sites of these deposits, these elements include scandium and probably yttrium and lanthanoids, i.e., rare and disseminated elements, whose valent state remains constant in the natural redox potential range.

Generally, one can classify as geotechnological accessory elements in deposits mined by sulfuric acid underground lixiviation all those rare and disseminated chemical elements whose compounds are soluble in a sulfuric acid medium, especially those that form stable sulfate complex ions. Strong sulfate complexes with a stability constant of $>10^3$ are formed by Ba, Be, Bi, Cd, Ce, Cr, Dy, Er, Eu, Id, Hf, Hg, Ho, In, La, Lu, Ni, Pb, Pr, Sc, Sm, Tb, Th, Ti, Tm, U, Y, Yb, Zr. The strongest complexes with stability constants of $>10^6$ are formed by Zr, U, Tm, Th, Sc. This suggests the importance of separate studies toward selection of

lithogenetic rock types and their facies and geochemical varieties, and a search for effective reagents to be used in profitable extraction of rare and disseminated chemical elements from water-permeable rocks. Essentially, studies are needed to assess the possibility of extraction of new types of mineral resources found in amounts quite different from the usual ore-forming concentrations.

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